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# Canadian Journal of Research

*Issued by THE NATIONAL RESEARCH COUNCIL of CANADA*

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## A PRELIMINARY INVESTIGATION OF THE MANNER OF REMOVAL OF LIGNIN FROM SPRUCE IN CONCENTRATED SODIUM HYDROXIDE SOLUTIONS<sup>1</sup>

By L. S. MACKLIN<sup>2</sup> AND O. MAASS<sup>3</sup>

### Abstract

An apparatus and method have been devised for studying the cooking of wood with sodium hydroxide solutions. The apparatus was so designed that the amount of wood was smaller, and temperature, pressure and concentration of cooking liquor could be controlled more accurately, than heretofore. Wood samples of known bone-dry weight were then treated under fixed and reproducible conditions. The cooking of small spruce chips at 160° C. has been investigated for time periods up to three hours and using 20, 25, 29, 32 and 40% sodium hydroxide solutions, a concentration region not previously investigated. The pulp produced contained a certain amount of lignin changed so as to be readily soluble in dilute alkali. This together with lignin contained in the final cooking liquor was estimated. The rate of solution of lignin in the liquor was found to vary as the inverse cube of the sodium hydroxide concentration in the range examined. A tentative hypothesis based on lignin being a lyophilic colloid has been put forward to account for the following generalizations which could be made with regard to the data obtained. (a) Lignin cannot be dissolved until it is changed into a "dilute alkali-soluble form". (b) Increase in concentration of sodium hydroxide acts in two ways; first, in increasing the amount of this form and, second, in preventing it from leaving the pulp proper.

### Introduction

In the commercial soda process for the manufacture of wood pulp, cooking liquor solutions containing 5 to 10% of sodium hydroxide by weight are employed. Investigations, such as those of Sutermeister (6), into the influence of variable factors showed that increase in the alkali concentration of the liquor is accompanied by decrease in the yield of pulp. However, in these studies concentrations much above 15% of sodium hydroxide were not tried, since even in this region the yield of pulp was too low to be profitable.

In 1930 Ross (3) showed that wood could be pulped satisfactorily with cooking liquor containing 40% of sodium hydroxide by weight. The use of alkali of this concentration was investigated further by Ross and Adlington

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada. This paper is constructed from part of a thesis to be submitted in partial fulfilment of the requirements for the degree of Ph.D.

<sup>2</sup> Postgraduate student at McGill University and holder of a bursary under the National Research Council of Canada.

<sup>3</sup> Macdonald Professor of Physical Chemistry, McGill University.

(1, 4). The pulp yields were quite good, showing that the influence of concentration upon yield must suffer a change of sign at some value of the concentration intermediate between the lowest and the highest. Ross (3) found however that cooking with 40% alkali gave results quite different from those obtained with solutions of the usual strength. Apart from the differences in character of the pulps produced, there was a marked difference in the manner in which the lignin was removed from the wood.

Thus in the ordinary process, with dilute alkali, the lignin is removed continuously during the cooking. If the wood residue is taken from the liquor and thoroughly washed to remove sodium hydroxide, it may be dried and analyzed by one of the empirical methods for estimating lignin. Provided the cooking treatment has been sufficiently severe, say six hours at 170° C., the pulp is found to contain very little lignin. If the cooking liquor, a dark colored solution, be acidified, a heavy brown precipitate appears and may be filtered off, washed and dried. This amorphous substance, although undoubtedly different from lignin as present in the original wood, corresponds in amount, within a few per cent, to the loss of lignin from the wood. It is called alkali-lignin, and has been the subject of much research.

With 40% sodium hydroxide, Ross (3) obtained the following markedly different effects. In the first place the cooking liquor was pale yellow in color instead of red-brown. Deep coloring, however, was found in the water with which the pulp was washed. The pulp contained very little lignin, as did also the cooking liquor. On acidification of the liquor no precipitate was thrown down. The missing lignin was found in the alkaline wash water. Ross remarked, "It was found that the ligneous incrustations were insoluble in the cooking liquor, though changed to the extent that they were readily dissolved by liquor below 20 percent NaOH by weight at any temperature."

A search of the literature failed to reveal any reference to the use of sodium hydroxide solutions of concentrations intermediate between 20 and 40%. Ross considered that at some concentration between that used in the commercial process and 40%, a sharp transition from the usual behavior to that typical of 40% solutions would be found. The present investigation was undertaken with the purpose of obtaining more complete data on the influence of concentration upon the manner of removal of the lignin.

In an investigation of the soda cooking reaction the chief variable factors which may be considered are temperature, concentration of sodium hydroxide, and time of cooking. In the present work it was found possible to study only one temperature, 160° C., throughout the concentration range from 20 to 40% sodium hydroxide, for various time periods up to three hours.

#### Apparatus

The charges of wood were cooked in a small digester of special design. It was desirable to use a small digester in this work so that at the start of an experiment the required cooking temperature could be attained very rapidly. The long "heating-up" period of commercial cooks was thus eliminated. At the same time it was necessary to maintain the alkalinity of the cooking



liquor as nearly constant as possible during an experiment. To this end, fresh liquor was introduced into the digester at frequent intervals, while the spent liquor was withdrawn at a corresponding rate.

The details of the apparatus may be understood more clearly by referring to the diagrams. The cell or digester (Fig. 1) in which the wood was cooked was formed from an Allegheny steel tube (marked 1 in the diagram): internal diameter, 2 in.; external diameter,  $2\frac{1}{2}$  in.; height,  $1\frac{7}{16}$  in. This tube was clamped between two  $\frac{1}{4}$ -in. Allegheny steel plates (2, 2). Each of these plates was drilled and tapped to take a  $\frac{1}{8}$ -in. short iron nipple (3, 3). By means of  $\frac{1}{8}$ -in. iron tees (4, 4) and steel compression fittings (5, 5), two copper tubes (6, 6) were made to connect with the opening through each plate. The couplings of the compression fittings were turned from  $\frac{1}{2}$ -in. mild steel rod, bored to take  $\frac{1}{8}$ -in. copper tubing and threaded for  $\frac{1}{8}$ -in. I.P.S. caps. The caps were also bored to take  $\frac{1}{8}$ -in. copper tubing. Instead of cones, ordinary graphite packing was wrapped around the tubes.

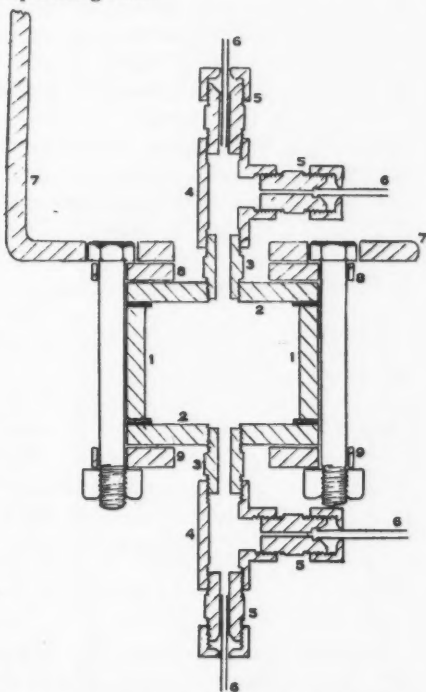


FIG. 1. Cross-section diagram of the digester.

The cell was formed from these parts by clamping the two plates over the ends of the tube, as shown in the diagram. Lead gaskets were inserted between the steel surfaces, so that the cell could be made tight. The cell was clamped together and supported in the following way. A heavy angle bracket (7) made from  $\frac{1}{4}$ -in. iron plate,  $3\frac{1}{2}$  in. wide, was bolted firmly to the wooden frame of the apparatus. The horizontal part of this bracket was 5 in. long, and made therefore an immovable flat plate, 5 in. long by  $3\frac{1}{2}$  in. wide by  $\frac{1}{4}$  in. thick. To the under side of this plate a steel disk (8),  $3\frac{1}{4}$  in. in diameter by  $\frac{1}{4}$  in. thick, was fastened by four  $\frac{3}{16}$ -in. bolts. These bolts are not shown in the diagram. The plate and disk were then bored to take four  $\frac{3}{8}$ -in. bolts  $3\frac{1}{2}$  in. long, the hexagonal heads being countersunk through the upper plate. These holes were placed symmetrically on a circle 3 in. in diameter. A large hole,  $1\frac{1}{4}$  in. in diameter, was also bored through the plate and disk, in a position central with regard to the four smaller holes. A second  $3\frac{1}{4}$ -in. disk was made (9), and bored with a  $1\frac{1}{4}$ -in. hole in the centre and four  $\frac{3}{8}$ -in. holes at the edges. This disk was then fitted on to the ends of the four heavy bolts. Then the upper

cell cover was fitted under the plate and disk, the tee and compression fittings protruding upwards through the large hole. The lower cell cover was placed similarly with regard to the lower disk, and the cell tube then fitted between the two cell covers. Hexagonal nuts were screwed onto the bolts, and the three parts of the cell were drawn tightly together. Once assembled, the dismantling and reassembling of the cell were very simple procedures, since they required only the removal and replacement of the cell tube.

To facilitate the charging of the cell with the small chips of wood used in this work, a small copper gauze cage was made and fitted permanently into the cell tube. The cage was cylindrical in shape, the sides being made of finely perforated copper sheet, and the bottom being a coarse copper wire netting. The chips of wood were packed into this cage and covered with a circular piece of metal gauze.

A diagram of the various connections leading to and from the cell is given in

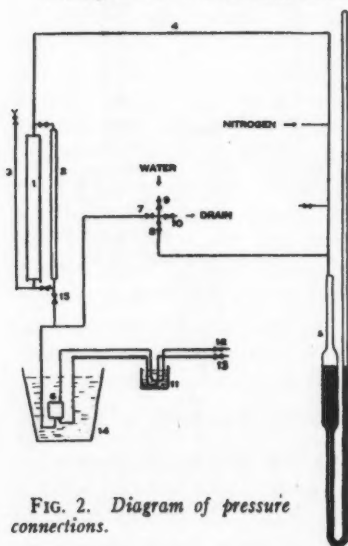


FIG. 2. Diagram of pressure connections.

Fig. 2. A reservoir (1) capable of holding sufficient cooking liquor for the performance of one experiment was made from a piece of 2-in. black iron pipe, 23 in. long. This was fitted with a gauge glass (2) and a side tube (3) to facilitate filling. Since it was necessary to introduce the cooking liquor into the cell under pressure, the top of the reservoir was connected by a pipe line (4) to a cylinder of compressed nitrogen. The pressure was regulated by a reducing valve on the cylinder, and was measured by a simple compression manometer (5). The bottom of the reservoir was connected to one of the copper tubes from the lower side of the cell (6). This inlet was connected also to the water-main, to the nitrogen line, and to the drain (valves 7, 8, 9, 10). The other copper tube from the lower side of the cell, and one from the upper side, were led

through a cold water bath (11) and served as outlets for the cooking liquor (valves 12, 13).

The temperature of the cell was controlled by having it immersed in a thermostatically controlled oil bath (14). The heating, stirring, and regulating were done electrically.

A galvanized pail formed the container of the bath, and this was suspended by ropes which passed over pulleys and carried a counterpoise. The bath was thus easily raised and lowered.

### Experimental

The wood was used in the form of small flat chips, about 2 cm. long in the fibre direction, 1 cm. wide and 2 mm. thick. This form was found to be more

satisfactory than coarse shavings, since about ten grams of chips could be packed into the cell, as compared with only seven grams of shavings. Thin cross sections, say 2 mm. in fibre length, were also tried, but were found to be unsatisfactory on account of the difficulty of straining the short fibred pulps produced by them. A considerable quantity (a few pounds) of these chips was made up at one time from a piece of black spruce. The moisture content of these chips was determined by drying a weighed sample at 105° C. for several days, and re-weighing. The supply of chips was kept in a stoppered bottle, and the moisture content of the wood was found to change very little: in seven weeks it decreased from 6.42 to 6.10%. The sample of wood to be used in an experiment was weighed out in the ordinary condition, without drying, and the actual bone-dry weight calculated from the known moisture content.

The caustic solutions were made up from ordinary c.p. sodium hydroxide sticks, the concentration being determined in each case by titrating a weighed sample with normal hydrochloric acid.

In making an experimental "cook", the following procedure was used.

The weighed sample of wood (about ten grams) having been introduced into the cell and the clamping bolts made tight, valves 12, 13 and 15 were closed and a high nitrogen pressure, say 120 pounds, applied through valves 7 and 8 (Fig. 2). Any rapid leak in the cell or cell connections was then readily found, and could be repaired. The nitrogen pressure was released and the reservoir filled with sufficient soda liquor for the performance of the experiment in hand.

The oil bath was heated up to the required temperature before the cell was immersed in it. This was done by raising the pail a few inches from the floor and heating it with Meker burners. It was found necessary to have the bath about 5° C. hotter than the proposed temperature of the experiment, to compensate for the cooling effect of plunging the cold cell into the oil. Generally half an hour was required to raise the temperature to the desired point.

Five or ten minutes before the experiment was to start, valves 7, 12 and 15 were closed, and the cell was evacuated by connecting outlet 13 to the water pump. This evacuation was performed merely to prevent the occurrence of air bubbles in the spaces between the chips when the liquor was forced into the cell.

The bath was then run up and the cell immersed in the oil; the heater and stirrer were started and the burners extinguished. After a lapse of one minute, in which time the cell was assumed to have acquired the temperature of the bath, valve 13 was shut and liquor introduced through valve 15 under a nitrogen pressure sufficient to prevent boiling.

From this point, quantities of the liquor (25 to 50 cc.) were withdrawn at five-minute intervals, so as to keep the alkalinity of the cooking liquor as close as possible to that of the original solution. The alkalinity of the effluent liquor was determined approximately from time to time by titrating a 1-cc. sample with normal hydrochloric acid. If the titre fell markedly below that of the original solution a larger quantity of liquor was withdrawn from the cell, and so on. The effluent liquor was collected in a covered flask.

At the end of the experiment valve 15 was closed, the heaters and stirrer turned off, and the oil bath lowered away from the cell. Then, as rapidly as possible, the pail of oil was replaced by one of cold water, and the latter run up until the cell was completely immersed. In a few minutes the cell was quite cold, and the pail of water was removed. The liquor in the cell was then blown out as follows. On opening valves 12 and 13 a little liquid flowed out of its own accord. These valves were then shut and nitrogen introduced into the cell under pressure. On shutting valve 7 and opening 13 the gas in the cell was able to expand and force the liquid through the outlet.

The cell having been emptied of liquor so far as possible, it was dismantled and the pulp removed to a large beaker. The experiment proper was now complete. Investigation of the pulp and liquor remained to be carried out, and this was done as follows.

The pulp, being still associated with an excess of cooking liquor, had to be treated, before drying, by some method which would remove the alkali and at the same time have as little effect as possible on the lignin content of the pulp. Now since, as Ross (3) showed, the treatment of wood with strong alkali solutions leaves a considerable proportion of the lignin in a changed condition, so that it is soluble in cold dilute alkali, it was necessary to avoid if possible the dilution of the alkali in contact with the pulp. The only way to do this, apparently, was to transform the sodium hydroxide into a sodium salt which could then be washed out with water. The pulp in the large beaker was therefore stirred up with a mixture of 30 cc. of concentrated hydrochloric acid and 700 cc. of water. The stirring was accelerated by the use of a small "Dumore" disintegrator (Type 6). This procedure, however, gave rise to a complicating factor, in that the neutralization was accompanied by the appearance of a white gelatinous precipitate. This precipitate was readily separated from the pulp by straining through a Büchner funnel, which retained the pulp, but allowed the precipitate to pass through with the liquid. The pulp was removed from the funnel and stirred up with about 700 cc. of hot water. It was then collected on the Büchner funnel and washed repeatedly with hot water. This washing generally resulted in further separation of precipitate from the pulp. The acid filtrate and washings were combined, giving 2 to 3 litres of liquid, and set aside for investigation of the precipitate. The pulp was placed in a weighed aluminium container and dried at 105° C. for several hours.

The precipitate in the acid wash, although very fluffy in appearance, settled rapidly to the lower part of the container. In one of the first experiments a small quantity of this precipitate was transferred by means of a tube to a glass slide, and examined under the microscope. Apart from a little cellular debris and a few stray fibres the mass had no structure discernible even with the oil immersion lens. Hertzberg's solution stained the cellular matter blue, the amorphous matter yellow, indicating that the former was cellulose, the latter lignin. The precipitate was not stained red by phloroglucinol, however, and was therefore not "unchanged lignin". Taking into account the manner of formation and the appearance of the precipitate it seemed reasonable to suppose that it was simply alkali-lignin which had been clinging loosely to the fibres

and which was separated from them when the fibres were torn apart in the disintegration of the pulp. In any case, whatever was the source of this substance, it was necessary to determine the amount of ligneous material in it, and this was done in the following way.

The acid washings and precipitate were heated on the steam bath until the volume had been reduced to about 500 cc. This generally took about 24 hr. and rendered the precipitate darker and somewhat granular. The hot liquid was then poured through a fluted filter paper (11 cm.) in an ordinary funnel, and the precipitate washed with a little water. After draining, the paper and precipitate were transferred to a small beaker, and the lignin content estimated by the method of Ross and Potter (5).

The pulp, after thorough drying, was weighed, and from the calculated bone-dry weight of the original wood the percentage yield obtained. Samples of the pulp were then analyzed for lignin, and for solubility in 1% sodium hydroxide. The extraction with a 1% alkali dissolves out any "changed lignin", *i.e.*, lignin which, although not dissolved by the cooking, is nevertheless altered in such a way that it may be dissolved by dilute alkali, even in the cold. The extraction was carried out in the standard way, as described in text books on wood. To determine how much "changed lignin" was contained in the pulp, a sample of the extracted pulp was then analyzed for lignin in the usual way. The difference between the lignin content of the original pulp and that of the extracted pulp gave, therefore, the quantity of "changed lignin" in the pulp.

There now remained for consideration only the cooking liquor. This was always of a yellow color, the shade being deeper the lower the concentration of alkali. It always contained, however, a considerable amount of thick dark green precipitate, which appeared only after standing, and which collected at the top of the liquid. The precipitate dissolved in acids, and was consequently assumed to be non-ligneous in nature. As the scope of this work required only a knowledge of the quantity of alkali-lignin in the liquor, no further attempt was made to determine the character of this precipitate.

The liquor was thoroughly shaken and poured into a measuring cylinder. The total volume was recorded, and an aliquot portion, 100 cc., pipetted into a beaker and diluted with an equal volume of water. Concentrated hydrochloric acid was then added until the mixture was strongly acid. At the neutral point the solution became quite clear and nearly colorless. The absence of precipitate at this stage, however, did not indicate that there was no alkali-lignin present, for when the solution was heated for a few hours in a covered beaker on the steam bath, the liquid became cloudy and finally a gelatinous light brown precipitate was formed. This was filtered off; washed, and analyzed for lignin in the same way as the precipitate from the acid wash. From the result, the quantity of lignin which could have been obtained from the whole cooking liquor by this method was calculated, and this amount taken as representing the lignin actually dissolved in the cooking.

In brief, the performance of such an experimental cook and its attendant analyses provide the following data:



A sample of wood, the bone-dry weight of which is known, has been treated under definite temperature and pressure conditions for a definite length of time with liquor of approximately known strength. As a result of this treatment a quantity of pulp has been produced containing a definite amount of lignin. Of this lignin a certain quantity has been so changed that it is readily dissolved by dilute alkali: this fraction is known. At the same time a certain quantity of lignin has been dissolved from the wood by the cooking liquor. Finally, an amount of lignin has been split off from the pulp in the washing process; this is changed lignin, and should be considered, presumably, along with the changed lignin in the pulp.

Such a set of data was obtained for each of 20 different experimental cooks. In this series, at the one temperature,  $160^{\circ}\text{C}.$ , a range of four different time periods and five different concentrations of sodium hydroxide was covered. Not every experiment was repeated, but a number of repetitions were made, and the results of these generally agreed fairly well with those of the original experiments. The best agreement was obtained with the data for the lignin content of the extracted pulp and the amount of lignin dissolved in the liquor. As will be seen shortly, it was these two quantities which were found to display definite relations with concentration and time of cooking.

### Results

The analytical results are given in Table I. All values are expressed in relation to the bone-dry weight of the original wood taken as 100%. Included with them are certain combinations of the original data:

The "total cooking" or "total delignification",  $D$ , represents the difference between the lignin content of the original wood and that of the pulp after extraction with dilute alkali.

The ratio of the amount of the lignin in the liquor,  $L$ , to the total delignification,  $D$ , is interesting. It represents the fraction of the lignin, available for solution, which has actually been dissolved.

The ratio  $D/(D-L)$  was found to display interesting variations with variation in the concentration of sodium hydroxide.

### Discussion of Results

If now the values of the lignin in the liquor,  $L$ , are plotted against the corresponding cooking times, the graph shown in Fig. 3 is obtained. Within the limits of experimental error, the points lie on a straight line

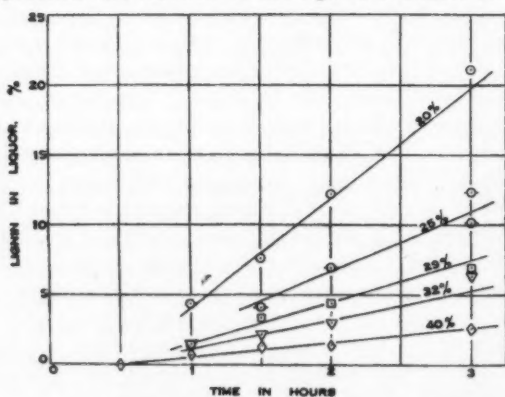


FIG. 3. Graph showing the relation between the quantity  $L$  and the cooking time for different concentrations of sodium hydroxide.

TABLE I  
EXPERIMENTAL RESULTS

Time of cooking, hr.	Concentration of NaOH in cooking liquor, %				
	20	25	29	32	40
Lignin in original pulp, %					
1	20.8	17.1	15.4	15.4	13.9
1.5	17.1	11.7	17.1	17.2	9.1
2	10.4		14.9	18.0	
3	10.5	12.3	8.5	11.3	10.4
	6.7	6.3	11.0	12.1	9.6
		7.4			
Lignin in acid wash, %					
1	1.2	5.4	11.6	5.4	9.2
1.5	3.3	6.2	6.0	6.3	12.7
2	5.4		5.6	3.6	
3	0.8	3.1	10.3	7.9	8.4
	2.1	9.9	5.2	6.1	7.7
		7.8			
Lignin in liquor, % (L)					
1	4.3		1.4	1.7	0.7
1.5	7.6	4.0	1.4	1.4	
2	7.7		3.3	2.1	1.3
3	12.2	6.9	4.3	2.9	1.4
	21.0	10.9	6.9	6.3	2.5
		10.2			
Lignin in extracted pulp, % (e)					
1	13.0	10.5	8.6	4.9	1.9
1.5	6.3	6.1	9.4	5.9	
2	5.5		4.4	3.6	1.8
3	4.0	4.0	3.5	1.9	1.0
	1.7	2.3	0.9	1.2	0.5
		2.7			
Total cooking, % (D), (29-e)					
1	16.0	18.5	20.4	24.1	27.1
1.5	22.7	22.9	19.6	23.1	
2	23.5		24.6	25.1	27.2
3	25.0	25.0	25.5	27.1	28.0
	27.3	26.7	28.1	27.8	28.5
		26.3			
Ratio L/D					
1	0.268		0.070	0.066	0.026
1.5	0.333	0.175	0.134	0.084	0.048
2	0.488	0.276	0.169	0.107	0.050
3	0.770	0.396	0.246	0.228	0.088
Ratio D/(D-L)					
1	1.37		1.07	1.07	1.03
1.5	1.50	1.21	1.15	1.09	1.05
2	1.95	1.38	1.20	1.12	1.05
3	4.35	1.66	1.32	1.29	1.12



for each of the different concentrations. Therefore the rate of solution of lignin in the liquor is a constant for any given concentration of sodium hydroxide.

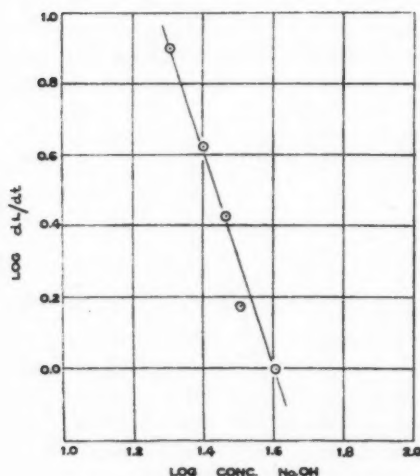


FIG. 4. Graph showing the logarithmic relation between the rate of solution of lignin and the concentration of sodium hydroxide.

In fact, if the logarithm of the rate (the logarithm of the slope of the line) is plotted against the logarithm of the concentration, a straight line is obtained, as shown in Fig. 4. This indicates that the rate of solution of lignin in the liquor,  $dL/dt$ , is related to the concentration of sodium hydroxide,  $c$ , by the equation

$$dL/dt = K_1 c^n$$

The value of  $n$  is found to be very nearly  $-3$  ( $-3.05$  as calculated).

The fact that the amount of lignin actually dissolved in the liquor may be only a small fraction of the total delignification, and the fact that the amount of lignin going into solution increases with time, even when the total delignification is complete, suggests that the solution of the lignin in the liquor takes place in two stages. Thus the first reaction may

be a conversion of the original lignin into a form which is completely soluble in dilute alkali. This changed lignin is then gradually acted upon by the liquor and goes into solution or fine suspension. The rate at which the first reaction proceeds is much higher at higher concentrations of sodium hydroxide. This can readily be seen by plotting total delignification against time of cooking, as shown in Fig. 5. On the other hand, the rate at which the second reaction proceeds, *i.e.*, the rate at which the changed lignin is dispersed in the liquor, must decrease very rapidly with increase in concentration of sodium hydroxide.

If the solution of lignin does take place in two stages, then the amount of lignin finally obtained in solution should be considered as a fraction of the amount changed. If this

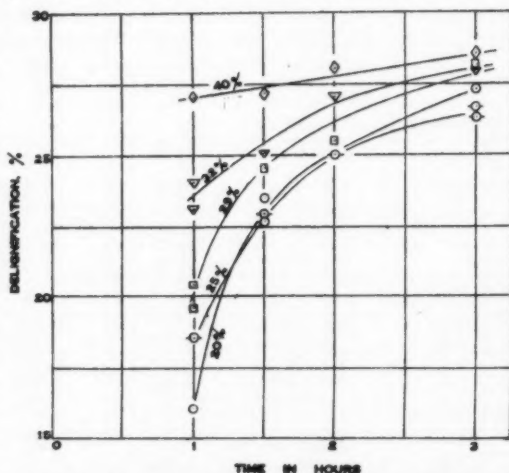


FIG. 5. Graph showing the relation between the quantity  $D$  and the cooking time for various concentrations of sodium hydroxide.

fraction, the amount of lignin in the liquor divided by the total delignification, be plotted against cooking time, the graph shown in Fig. 6 is obtained. Again, within the limits of experimental error, straight lines are obtained for the different concentrations of sodium hydroxide. Now in the case of the values of  $L$  considered apart from those of  $D$ , it may be seen in Fig. 3 that the straight lines appear to converge to a point on the time axis at or near the 0.5-hour period. This suggests that no lignin goes into solution in the liquor during the first half hour of cooking, regardless of the concentration of sodium hydroxide. Such a time lag might be explained as representing the time required for complete permeation of the wood with liquor and opening up of the wood structure.

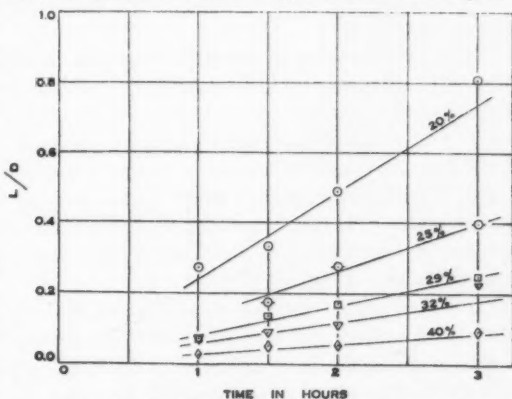


FIG. 6. Graph showing the relation between the ratio  $L/D$  and the time of cooking, for different concentrations of sodium hydroxide.

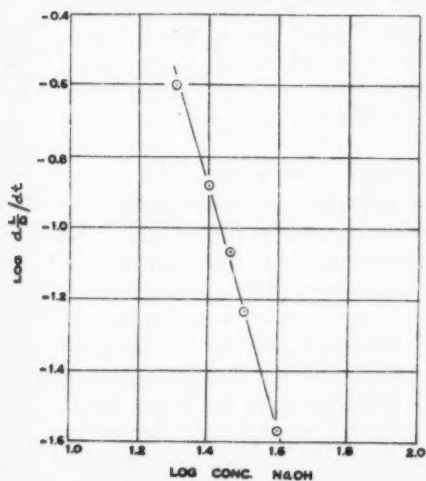


FIG. 7. Graph showing the logarithmic relation between  $d\frac{L}{D}/dt$  and the concentration of sodium hydroxide.

The fact that the rate of solution of the changed lignin decreases so rapidly with increase in sodium hydroxide concentration suggests that the second reaction is a fine colloidal dispersion rather than a true solution of products formed by chemical decomposition of the lignin.

On the other hand the straight lines obtained by plotting  $L/D$  against  $t$  (Fig. 6) appear to converge toward the origin. This confirms the idea that lignin cannot be dissolved in the liquor until it is changed into the "dilute alkali-soluble" form. Now if the slopes of these lines be calculated, and the logarithms of the slopes plotted against the logarithms of the sodium hydroxide concentrations, another straight line is obtained, as shown in Fig. 7. In terms of symbols,

$$\frac{d\frac{L}{D}}{dt} = K_2 c^n,$$

where  $n$  is again very nearly  $-3$  ( $-3.11$  as calculated).

The fact that the rate of solution of the changed lignin decreases so rapidly with increase in sodium hydroxide concentration suggests that the second reaction is a fine colloidal dispersion rather than a true solution of products formed by chemical decomposition of the lignin.

It may now be of value to recapitulate and extend the conclusions drawn from the experimental results.

(1) With increasing concentration of sodium hydroxide the total delignification is increased.

(2) By the cooking of wood the lignin is obtained in a "colloidally soluble" form, but increase in the concentration of sodium hydroxide retards the dispersion of this lignin.

(3) This "colloidal" form of lignin is gradually acted upon by the sodium hydroxide, giving micellae which are more easily dispersed.

(4) The changed lignin in wood cooked with strong alkali cannot be peptized in pure water. It can, however, be peptized successfully in solutions of sodium hydroxide. Subsequent acidification and heating of the solutions result in reprecipitation of the lignin.

(5) The micellae of these sols may not consist altogether of unchanged lignin. They may represent a more or less hydrated derivative. The fact that part of the lignin is definitely changed in the cooking process is brought out by the difference generally found between the total lignin estimated after cooking and the lignin content of the original wood.

Colloidal lignin is a substance, presumably, of the lyophilic type. General information on lyophilic colloids may be found in text books on colloid chemistry, such as that of Freundlich (2). On the basis of such information, the following generalizations can be made: In salting out, lyophilic substances separate at high concentrations of alkali salts (several times molar). With alkalis such as sodium hydroxide, separation occurs only at very high concentrations. The substances come out generally in the form of amorphous flakes. The process is reversible; by dilution of the solution the separated matter can be redissolved.

In the present instance the behavior of the lignin is certainly similar to this. Thus the higher the concentration of sodium hydroxide the more difficult it is for the lignin to be dispersed. This effect is the opposite of salting out. The

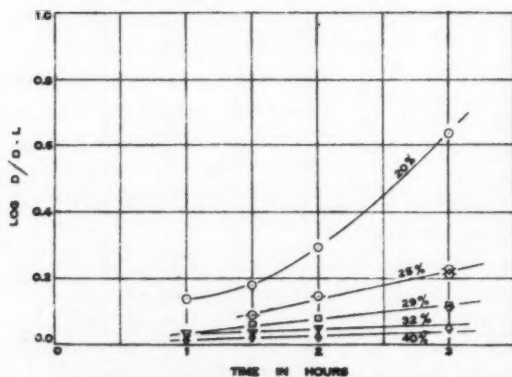


FIG. 8. Graph showing the relation between the quantity  $\log D/(D-L)$  and the time of cooking, for different concentrations of sodium hydroxide.

fact that the lignin continues to go slowly into solution, even at the highest concentrations of sodium hydroxide, is to be interpreted as due to the continued breaking up of the larger micellae. Thus although most of the changed lignin may be in the form of micellae for which the sodium hydroxide concentration is sufficiently high to produce complete salting out, these micellae may be gradually broken up into smaller particles for which the alkali solution does not exert a salting out action.

If the logarithms of the ratios,  $D/(D-L)$ , be plotted against cooking times, straight lines are obtained for all concentrations of sodium hydroxide except the lowest (20%), as shown in Fig. 8. This indicates possibly the critical nature of this concentration, since below it the solution of lignin proceeds hand in hand with total cooking.

Throughout this discussion no reference has been made to the chemical nature of lignin or to the chemical reactions involved in cooking. The present work represents an attempt to follow lignin, considered in a general way, through different phases of a cooking process.

### Acknowledgment

The authors are indebted to the Pulp and Paper Division of the Forest Products Laboratories of Canada for the inclusion of this work in its program of research where the necessary apparatus was provided.

To Dr. J. H. Ross the authors are greatly indebted for many valuable suggestions and for the interest he showed during the whole course of the research.

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PREPARATION OF THE ETHERS OF VINYL ALCOHOL<sup>1</sup>BY WILLIAM CHALMERS<sup>2</sup>

## Abstract

The simple vinyl alkyl ethers are readily prepared from the  $\beta$ -bromo-ethyl ethers by the action of solid sodium hydroxide. Besides the vinyl ethers, the dialkyl ethers of diethylene glycol are formed in these reactions.  $\beta$ -Bromoethers are obtainable from the mono-ethers of ethylene glycol through the use of phosphorus tribromide. The constants of several vinyl ethers are given for the first time. The preparation of vinyl methyl ether, a gas at room temperature, and of vinyl *n*-butyl ether, b.p. 93.3° C., is described.

The following paper describes the results of a search for a convenient laboratory preparation of the vinyl alkyl ethers. The method developed proved suitable for the obtaining of desirable quantities of vinyl ethyl and butyl ethers. It led also to the preparation of vinyl methyl ether, although in small yield. The  $\beta$ -chloro-ethyl and phenyl ethers were prepared for the purpose of comparison.

Vinyl ethyl ether was first described by Wislicenus (17) who made it the object of an extensive study. At the time the present investigation was commenced the only reference to the existence of any other alkyl ether of vinyl alcohol lay in a patent specification (13)\*. This did not give even the boiling points of the ethers quoted as examples (propyl and isopropyl). Besides the ethyl ether, divinyl ether (see 8) and two aromatic ethers (14) had been mentioned in the literature but on these also information was very scanty.

Since the discovery of vinyl ethyl ether there has been no dearth of announcements of new reactions in which it is formed. Wislicenus' original procedure was too laborious to be practicable. The one usually described in the standard textbooks has been developed by Claisen (3) and depends upon the possibility of extracting alcohol from diethyl acetal,  $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$ , to give the unsaturated ether. Phosphorus pentoxide, in the presence of quinoline, is used for this purpose. The method is rather unsatisfactory, not only on account of the low yield, but also because of the difficulty encountered in effecting a complete separation of the vinyl ether and unchanged acetal.

The addition of alcohols to acetylene, in a manner analogous to the commercial preparation of the vinyl esters, would seem to be the most direct manner of preparing the vinyl ethers. Nevertheless, it appears from the patent literature that, by substitution of alcohol for the acids in the process, the product is almost entirely acetal (4).

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Contribution from the Department of Chemistry, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada. Constructed from a thesis submitted to McGill University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, April 1930.

<sup>2</sup> Holder of scholarships under the National Research Council of Canada, 1927-1931, at McGill University, Montreal, Canada, and at the University of Freiburg, Germany.

\* Abstracts of two new patent-processes have appeared since the present work was completed. One of these depends upon the reaction of the vinyl halides with the alcoholates of the alkali and alkaline earth metals (9, 10). Another utilizes the catalytic action of metals of the first or eighth group in decomposing the acetals (11).

Vinyl phenyl and *p*-tolyl ethers have been made by Powell and Adams (14, p. 648) by distillation of the readily obtainable phenyl and tolyl  $\beta$ -bromo-ethyl ethers over powdered sodium hydroxide.

If it were possible to eliminate a molecule of water from the molecule of a mono-alkyl ether of ethylene glycol by the hypothetical reaction:  $\text{CH}_2\text{OHCH}_2\text{OR} - \text{H}_2\text{O} \longrightarrow \text{CH}_2\text{:CHOR}$ , a convenient preparation of the vinyl ethers would be at hand. A number of attempts to bring about this change directly in the case of the ethyl ether were fruitless. The utilization of the (now very cheap) glycol mono-ethers is possible, however, by their conversion into the  $\beta$ -halogenated ethers. Alkyl  $\beta$ -bromo-ethyl ethers were found to be readily converted into the vinyl derivatives by treating with solid sodium hydroxide at their boiling points.

It was necessary to devote attention not only to the reaction of the halogenated ethers with alkalis but also to their preparation from the glycol ethers. The hydroxyl group present in these compounds cannot be esterified by means of concentrated halogen hydracid as in the case of the simple alcohols, owing to the great ease with which their alkoxyl group is hydrolyzed. Phosphorus trichloride had been employed for this purpose by Karvonen (12, p. 1269) but the use of the tribromide had not apparently been tried. In fact, the only method of preparing the simple  $\beta$ -bromo-ethyl ethers described in the literature seems to be an indirect and tedious one described by Karvonen (12, p. 1269). Study of the reaction of phosphorus tribromide with the available glycol mono-ethers indicated that, while the yield of bromo-ether obtained from the monomethyl glycol ether was too small to be practicable, the ethyl and butyl  $\beta$ -bromo-ethyl ethers can be suitably prepared by its use.

The preparation of the vinyl ethers is carried out as follows: A distilling apparatus with fractionating column is set up, the flask is partly filled with coarse, dry soda-lime as bearer and the bromo-ether and a large excess of powdered sodium hydroxide added. The flask is then immersed in an oil-bath which is heated moderately so that the temperature registered by a thermometer in the still-head does not rise appreciably above the boiling point of the vinyl ether. In this manner the low-boiling product is continuously separated from the bromo-ether which is retained in the reaction flask. After two to three hours nothing more comes over. The crude vinyl ether is separated from the water which has distilled over with it and treated with a convenient drying agent. There is usually a little unchanged bromo-compound present, but, owing to a considerable difference in the boiling points, one distillation through a good column is sufficient to remove it practically completely. The yields of vinyl ether obtained from the methyl, ethyl and *n*-butyl  $\beta$ -bromo-ethyl ethers are somewhat higher than one third of the theoretical.

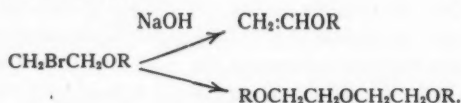
As the  $\beta$ -chloro-ethers are much cheaper to prepare than the corresponding bromo-derivatives, a process which permits of their use would possess a decided advantage. The simple, mono-substituted compounds proved to be remarkably inert to the action of caustic alkali even at high temperatures. The di-substituted  $\beta,\beta'$ -dichloro-diethyl ether gave good yields of vinyl



$\beta$ -chloro-ethyl ether with greater readiness. The possibility of decomposing this ether is to be ascribed to its elevated boiling point which provides a higher reaction temperature than in the case of the monohalogen compounds. For this reason, the reaction is found to proceed beyond the stage of the monovinyl ether with great slowness, divinyl ether being obtained only on long-continued heating\*.

The low reactivity of the  $\beta$ -halogenated ethers, particularly the chloro-compounds, is clearly demonstrated by the severe treatment necessary to make them part with their halogen. The Finkelstein test (7, p. 1529) shows complete inertness of the substituted chlorine and bromine to sodium iodide. Quinoline, even after prolonged heating, produces no observable dehalogenation. While it might seem preferable to employ the alkali in solution, some experiments with dichloro-diethyl ether showed that the use of alcoholic potash leads to the production of high-boiling products, apparently ethoxy-derivatives.

The low yields of vinyl ethers obtained from the alkyl bromo-ethyl ethers are not due, as might be supposed, to an incomplete action of the dehalogenating agent. It is caused, in each case, by a side reaction giving a high-boiling, liquid by-product. These may be isolated if, after the formation of vinyl compound has ceased, the fractionating column be replaced by a short connecting tube leading to the condenser and the flask be strongly heated. For example, in the preparation of vinyl ethyl ether, a considerable quantity of a colorless liquid can be obtained which distils within a range of a few tenths of a degree of  $186^{\circ}\text{C}$ . These substances were found to be the dialkyl ethers of diethylene glycol. The amounts formed corresponded to the proportion of bromo-ether which had not been converted into the unsaturated ether, namely about 60%. Thus the reaction of alkyl  $\beta$ -bromo-ethyl ethers with sodium hydroxide takes place in two directions:



The formation of diethylene ethers is probably to be explained by the intermediate production of the sodium derivatives of the glycol mono-alkyl ethers. These would react further with unchanged bromo-ether to give the diethylene glycol ethers. Secondary products of this nature are not obtained from the less reactive dichloro-diethyl and phenyl  $\beta$ -bromo-ethyl ethers.

The vinyl ethers prepared, with the constants determined, are shown in Table I.

With the exception of vinyl methyl ether, which is a gas at room temperature, these compounds are mobile liquids. They have an odor resembling somewhat that of similar allyl derivatives. They may be kept indefinitely, even in bright sunlight, without change. A distinctive property which serves as a

\*Hibbert and coworkers (8) have described the preparation of divinyl ether from dichloro-diethyl ether and noted the appearance of vinyl  $\beta$ -chloro-ethyl ether as an intermediate stage (8, p.1553).



TABLE I  
 CONSTANTS OF SOME VINYL ETHERS

Ether	Formula	Boiling point*, °C.	Density	Refractive index
Vinyl methyl	$\text{CH}_2\text{:CHOCH}_3$	(gas) 12-14		
Vinyl ethyl	$\text{CH}_2\text{:CHOC}_2\text{H}_5$	35.5	$D_4^{20} = 0.7589$ $D_4^{9.2} = 0.7723$	$n_D^{9.2} = 1.3856$
Vinyl <i>n</i> -butyl	$\text{CH}_2\text{:CHOC}_4\text{H}_9$	93.3	$D_4^{20} = 0.7887$	$n_D^{20} = 1.4026$
Vinyl $\beta$ -chloro-ethyl	$\text{CH}_2\text{:CHOCH}_2\text{CH}_2\text{Cl}$	108.0	$D_4^{20} = 1.044$	$n_D^{20} = 1.4362$
Vinyl phenyl	$\text{CH}_2\text{:CHOC}_6\text{H}_5$	155.5	$D_4^{20} = 0.9776$	$n_D^{20} = 1.5226$

\*The boiling points are all corrected.

convenient test is their almost explosive conversion into resinous polymeric forms on the addition of small amounts of iodine. A short study of these phenomena is described in the next paper (2).

#### Molecular Refractivities of the Vinyl Ethers

According to Eisenlohr (5), elements such as oxygen, which are capable of assuming a higher valency, cause anomalies in the refractivity when combined with another unsaturated group. Using the data given in Table I, calculation gives the molecular refractivities shown in Table II.

 TABLE II  
 MOLECULAR REFRACTIVITIES OF VINYL ETHERS, CALCULATED FROM DATA IN TABLE I

Ether	$M_D$		Differences
	Found	Theoretical*	
Vinyl ethyl	21.89	21.85	+ .04
Vinyl <i>n</i> -butyl	30.94	31.08	- .14
Vinyl $\beta$ -chloro-ethyl	26.65	26.71	- .06
Vinyl phenyl	37.49	36.72	+ .77

\*Calculated from the atomic refractivities given by v. Auwers and Eisenlohr (6, p. 605).

It is seen that the aliphatic ethers give values for the optical constant which do not differ appreciably from the theoretical. Only in the case of the phenyl ether, where the aromatic radical forms an extension to the chain of conjugated unsaturated systems, is a small but distinct exaltation evident.

### Experimental

#### Preparation of the $\beta$ -halo-ethers

The new reactions carried out were as follows:

- $\text{CH}_2\text{OHCH}_2\text{OCH}_3 \xrightarrow{\text{PBr}_3} \text{CH}_2\text{BrCH}_2\text{OCH}_3$  (B.p., 110° C.; yield, 10%)
- $\text{CH}_2\text{OHCH}_2\text{OC}_2\text{H}_5 \xrightarrow{\text{PBr}_3} \text{CH}_2\text{BrCH}_2\text{OC}_2\text{H}_5$  (B.p., 127° C.; yield, 50-58%)
- $\text{CH}_2\text{OHCH}_2\text{OC}_4\text{H}_9 \xrightarrow{\text{PBr}_3} \text{CH}_2\text{BrCH}_2\text{OC}_4\text{H}_9$  (B.p., 173-174° C.; yield, 37-43%)
- $\text{CH}_2\text{OHCH}_2\text{OC}_6\text{H}_5 \xrightarrow{\text{SOCl}_2} \text{CH}_2\text{ClCH}_2\text{OC}_6\text{H}_5$  (B.p., 153-154° C.; yield, 50%)

Only the butyl compounds are new. The yields are calculated on the assumption that the reactions in each case are simple replacement of hydroxyl by halogen. They seem actually to be much more complicated.

The action of a large excess of hydrobromic acid (constant boiling point) upon glycol mono-ethyl ether was investigated. A vigorous reaction took place giving, on heating, a distillate of ethyl bromide with a small proportion of ethylene bromide (identified by boiling points and densities).

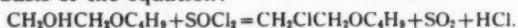
The preparation of the bromo-ethers is illustrated by the following example: *Butyl  $\beta$ -bromo-ethyl ether.* *n*-Butyl ether of ethylene glycol (810 gm., 7 moles), dimethyl aniline (300 cc., about 2 moles) and anhydrous ether (300 cc.) were placed in a two-litre, three-necked flask provided with a reflux condenser, stirrer and dropping funnel. The flask was cooled in ice and 200 cc. (slightly in excess of 2 moles) of phosphorus tribromide added dropwise with vigorous stirring. After the addition was completed, the mixture was heated on a water bath for several hours and allowed to stand overnight. It was then washed with much water and placed over potassium carbonate to dry. The solvent was separated by distillation, the crude bromo-ether coming over between 169-175° C. Yield, 427 gm. (37%).  $D_4^{17} = 1.222$ .

With smaller amounts a yield of 43% was obtained. The dimethyl aniline was added to remove the hydrogen bromide which was formed in considerable quantity.

Methyl and ethyl  $\beta$ -bromo-ethyl ethers were prepared in a manner quite similar except that, instead of tertiary amine, a large excess of the glycol ether was added. The reaction product in several cases was directly distilled without washing with water. When this is done, a thermometer must be inserted into the liquid itself and care taken that the temperature does not rise much above 240° C. Above 250° C. a violent decomposition sets in with the formation of free phosphorus.

*Ethyl  $\beta$ -chloro-ethyl ether.* This substance was prepared by allowing phosphorus trichloride to act upon glycol mono-ethyl ether. This preparation has already been carried out by Karvonen (12, p. 1269) who did not quote the yield he obtained. The writer succeeded in obtaining only 21% of the theoretical.

*n*-Butyl  $\beta$ -chloro-ethyl ether. This was prepared by the use of thionyl chloride, adopting a procedure similar to that employed by Bennett and Heathcoat (1) in making the ethyl ether. The yield given above was calculated on the basis of the equation:



#### *Preparation of the Vinyl Ethers*

It is not necessary to employ a copper flask in the preparation of the simple alkyl ethers as, under the conditions described, the alkaline mixture does not fuse.

The measurements of the densities of vinyl ethers were carried out by either a dilatometric or a direct-weighing (suspended-sinker) method. Except in the case of the ethyl ether, the indices of refraction were measured by means of an Abbé refractometer.

*Vinyl methyl ether.* From 26 gm. of methyl bromo-ethyl ether was obtained 4.5 gm. (approximately 40% yield) of the vinyl ether, following the general method described above. As the halogenated ether has a boiling point almost 100° C. higher than the vinyl ether, its separation offered no difficulty. The receiver was cooled in a freezing mixture and the material dried by sealing in a tube with anhydrous potassium carbonate. The boiling point was determined only approximately. A micro-gas analysis, made by Dr. E. W. R. Steacie, was unfortunately incomplete through an accident. It indicated, however, that the compound was quite pure: Calcd. for  $C_3H_6O$ ; vol.  $CO_2$ /vol.  $H_2O$  = 1.50 or  $C/H$  = 0.500; found vol.  $CO_2$ /vol.  $H_2O$  = 1.52 or  $C/H$  = 0.507.

The secondary product formed in this preparation, being very small in amount, was not examined.

On the analogy of Claisen's preparation for vinyl ethyl ether it might be expected that the action of phosphorus pentoxide on dimethyl acetal would lead to the formation of the methyl ether. An attempt to carry this out gave only a very small amount of a low-boiling liquid from which it was impracticable to attempt to separate any of the unsaturated ether formed.

*Vinyl ethyl ether.* Ethyl bromo-ethyl ether (400 gm.) was treated in three lots, the receiver being cooled with ice. After drying over potassium carbonate and fractionating, 83 cc. (63 gm., 33.5% yield) of pure ether of boiling point 35.4–35.6° C. was obtained.

The measurement of the refractivity of this compound was carried out on a goniometer using a hollow prism. The maximum attainable temperature was 9.2° C., owing to the rapid evaporation of the liquid.

The ethyl bromo-ethyl ether was refluxed for many hours with quinoline but no decomposition could be detected. Ethyl chloro-ethyl ether was refluxed for many hours with powdered sodium hydroxide, to which some sodium iodide had been added, but without appreciable decomposition of the ether. In order to elevate the temperature of the reaction, the same mixture was heated in an autoclave at 150° C. for several hours. Some vinyl ether was formed but only in very small yield. Another attempt was made by passing vaporized chloro-ether over soda-lime in a tube heated to 200–250° C., but again the yields were negligible. A small amount of a gas was generated. This was probably butadiene, as it is known that ethyl chloro-ethyl ether gives the diolefine when passed over soda-lime heated to a very high temperature (15, p. 49).

In attempting to dehydrate glycol mono-ethyl ether directly to the vinyl ether, several methods were tried. One of these consisted of distilling the glycol derivative over phosphorus pentoxide in the presence of an excess of carefully purified quinoline; another, of long refluxing over anhydrous zinc chloride. By the use of phosphorus pentoxide, only a very little low-boiling material was obtained. When zinc chloride was employed, some acetaldehyde and alcohol were formed, but no trace of vinyl ether could be observed. Distillation of the glycol ether in the vapor phase at moderate temperatures over several types of alumina, as well as thoria, led to extensive decomposition into acetaldehyde and alcohol, but gave no vinyl ether.

*Formation of diethyl ether of diethylene glycol.* The by-product obtained as described above in the preparation of vinyl ethyl ether, had a density of  $D_4^{20} = 0.907$ . It was completely soluble in five or six volumes of cold water. From its aqueous solution it could be salted out by the addition of potassium carbonate. Calcd. for  $C_8H_{18}O_3$ : C, 59.23; H, 11.19%. Found: C, 59.13, 59.00; H, 11.06, 11.00%.

For comparison a product of definite constitution was prepared in the following manner. The sodium derivative of the mono-ethyl ether of diethylene glycol ("carbitol") was formed by adding the calculated amount of sodium metal to a benzene solution of this compound. On treating this product with ethyl iodide, reaction took place smoothly. After purification, the resulting liquid had the constants: b.p.,  $186^\circ \text{C}$ .;  $D_4^{20}$ , 0.908. It resembled the other material in solubility, odor, and high viscosity.

*Vinyl n-butyl ether.* From 150 gm. of butyl bromo-ethyl ether, in two lots, 28.5 gm. (34% yield) of the vinyl ether was obtained. A considerable quantity of water came over and the temperature in the still-head remained practically constant at  $80^\circ \text{C}$ . The crude ether was dried over potassium carbonate and fractionated several times. Calcd. for  $C_6H_{12}O$ : C, 71.93; H, 12.09%. Found: C, 71.88; H, 12.02%.

*n-Butyl  $\beta$ -chloro-ethyl ether* was refluxed for six hours over powdered sodium hydroxide. After fractionating, about 7% of this compound was found to have been converted into the vinyl ether.

*Secondary product in the preparation of butyl ether.* This had a boiling point of  $245\text{--}247^\circ \text{C}$ . When heated with hydrobromic acid it gave a distillate which consisted largely of butyl bromide (b.p.,  $101^\circ \text{C}$ .), but also contained a small proportion of a liquid boiling between  $215\text{--}220^\circ \text{C}$ . (within which range lies the boiling point of diethylene glycol monobutyl ether). Its odor resembles that of the diethyl compound but its solubility in water is much less. The analysis agreed with that of dibutyl ether of diethylene glycol. Calcd. for  $C_{12}H_{26}O_3$ : C, 66.00; H, 12.00%. Found: C, 65.89; H, 11.87%.

*Vinyl  $\beta$ -chloro-ethyl ether.* This compound was obtained by treating  $\beta$ ,  $\beta'$ -dichloro-diethyl ether with powdered sodium hydroxide in the same manner as the bromo-ethers. By separation of the unchanged material and re-treating, a total yield of 70% was obtained. The temperature of the still-head was kept at  $110\text{--}120^\circ \text{C}$ ., and the heating prolonged for three hours. A few cc. of divinyl ether was also obtained. Analysis:— Calcd. for  $C_4H_7OCl$ : Cl, 33.3%. Found: Cl, 33.2%.

Measurements, made by Mr. H. Wyman, of the density of this compound at three temperatures gave, besides that quoted above:  $D_4^{25} = 1.038$ ;  $D_4^{30} = 1.032$ .

$\beta$ ,  $\beta'$ -Dichloro-diethyl ether was refluxed with alcoholic potash containing sodium iodide for several hours. The deposition of potassium chloride indicated that reaction had taken place. The bulk of the reaction product was a liquid distilling between  $180$  and  $210^\circ \text{C}$ . A little material boiling over the range  $75\text{--}115^\circ \text{C}$ . was obtained, but could not be fractionated to give a pure vinyl ether.

*Vinyl phenyl ether.* The preparation from phenyl bromo-ethyl ether has been already described by Powell and Adams (14, p. 648). In the present preparation, a yield of 33% vinyl ether was obtained in one distillation.

*Reactivity of the  $\beta$ -halogenated ethers.* To a 0.5-cc. portion of each of the chloro- and bromo-ethers prepared was added several cc. of pure acetone and 10 cc. of a 15% solution of sodium iodide in acetone. In no case was a precipitate of sodium chloride noticed even after standing for several days.

### Acknowledgment

This work was done in the course of an investigation of broader scope begun under the direction of Prof. G. S. Whitby, now of the National Research Laboratories, Ottawa. The writer wishes to thank Dr. C. F. H. Allen and other members of the staff of McGill University for their encouragement and advice.

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POLYMERIZATION OF VINYL ETHERS<sup>1</sup>BY WILLIAM CHALMERS<sup>2</sup>

## Abstract

A number of vinyl ethers investigated were found to undergo violent polymerization reactions on the addition of free iodine. With very small amounts of the catalyst, considerable differences in polymerizability are disclosed, the phenyl ether being least sensitive to its action. The alkyl ethers, but not the phenyl ether, are very slowly converted into polymeric forms under the influence of heat and ultra-violet light. The orders of polymerization of the products range from 18 to 82. The "mer" refractivities of some of the polymers have been determined and shown to agree with the theoretical values calculated on simple assumptions. A closed-ring chain structure, with the structural units arranged in regular order and joined by normal, single bonds, is proposed.

In a preceding paper (3) the preparation of several vinyl ethers of the general formula  $\text{CH}_2\text{:CHOR}$  has been described. In the following is given an account of some observations on the polymerization of these compounds under the influence of iodine, by heat, and by ultra-violet radiation.

In attempting to form the iodine-addition product of vinyl ethyl ether, Wislicenus (15, p. 113) discovered a reaction of an unusual nature. Although he did not get the expected di-iodide, a "balsamous" material was formed in a violent reaction on the addition of the halogen. When a very small proportion of iodine was added this was, indeed, taken entirely into true chemical combination, but the substance proved to be essentially a polymer of the original ether.

All the vinyl ethers studied in the present work, with the exception of divinyl ether, react with great violence on the addition of a quantity of iodine in excess of 0.5 to 5%, depending on the ether. The black, pitch-like products formed are in general soluble in all of the common solvents with the exception of the alcohols. When the iodine is employed in smaller proportions and in chloroform solution, much smoother reactions take place and the materials obtained are practically colorless.

Reduction of the amount of catalyst brings to light a large variation in the polymerizabilities of the different vinyl ethers. Thus, with 0.2% iodine, vinyl ethyl and vinyl *n*-butyl ethers are practically completely polymerized within 24 hr. but, even after six days, vinyl  $\beta$ -chloro-ethyl ether is only slightly affected and vinyl phenyl ether is unchanged. Vinyl ethyl and butyl ethers decolorize the added iodine solution immediately, become distinctly warm to the hand and remain so for several hours. In the case of the chloro-ethyl ether, the brown coloration takes 10 min. to disappear and the elevation of temperature is only slight. The vinyl phenyl ether never takes up completely even this small proportion of halogen and does not appreciably alter in temperature.

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<sup>2</sup> Holder of scholarships under the National Research Council of Canada, 1927-1931, at McGill University, Montreal, Canada, and at the University of Freiburg, Germany.



Wislicenus (15, p. 113) states that only a limited quantity of vinyl ethyl ether is polymerized by a definite amount of iodine. At least one part of the catalyst to 200 parts of ether is necessary to give complete polymerization, according to his work. If its action on the ethyl and butyl ethers has such a limit, it must be much lower than the value he gives. One part of iodine (in solution) was found to effect the entire conversion of 1000 parts of vinyl ethyl ether into polymer. This change required three days for completion. Vinyl  $\beta$ -chloro-ethyl ether shows, however, a definite limiting value. A quantity of this ether which had been sealed in a tube for 10 months with  $\frac{1}{208}$  part of iodine, still contained 16% of unchanged material. Under these conditions, then, only 175 parts of vinyl chloro-ethyl ether are polymerized by one part of catalyst.

The ready polymerizability of these ethers through the agency of a specific catalyst would lead us to inquire into their behavior under the influence of heat and light. If we were to adopt the same conditions of treatment that have been found sufficient in other well-studied groups of polymerizable compounds, such an inquiry would fail to detect any heat- or light-sensitivity. The period of heating must be extended to several months and exposure to a strong source of ultra-violet radiation must be carried on continuously for many days before a thermo- or photo-polymerization of the alkyl ethers becomes evident. Long-continued heating or irradiation by ultra-violet light is almost without action upon vinyl phenyl ether.

Vinyl chloro-ethyl ether showed exceptional behavior, as it was found to be completely converted into a polymeric form on heating for three days. It is probable that some hydrogen chloride is formed by partial decomposition of the ether and that this acts as a catalyst for the polymerization. The photo-polymerizability is practically the same as that of the butyl ether.

All the vinyl ethers prepared polymerize with explosive violence when treated with a trace of the volatile metallic halides. On the other hand, long contact with metallic sodium is without effect.

These ethers differ considerably from other groups of vinyl compounds in the nature of their polymerizability. Comparison with the closely related vinyl esters (4) shows that, in the absence of catalysts, the latter are much more readily photo- and thermo-polymerizable. It should be pointed out that while the phenyl group shares with acetyl, etc., the property of being more "negative" in character than the alkoxyl groups, it is precisely the aromatic ether which is least sensitive to heat or light. In connection with the agency of iodine in bringing about the polymerization of the vinyl ethers, it is of interest that *p*-vinyl anisol (13, p. 489) has also been found to be readily converted into a polymeric form on the addition of this catalyst. Sensitivity to iodine seems, therefore, to be a specific property conferred by the presence of an ether-oxygen atom which need not necessarily be in juxtaposition to the vinyl group.\* The accelerative effect of the halogen is in striking contrast to its distinctly

\*The polymerizations of unsymmetrical diphenyl ethylene (7) and cinnamylidene benzyl cyanide (12, p. 3403) have also been observed to be catalyzed by iodine but the action is much weaker and seems to be different in mechanism from that observed in the case of the ethers.



anti-catalytic action in the polymerization of other substances such as styrene\*, the vinyl halides (1, p. 321; 8, p. 1533), and methacrylic ester†.

### Nature and Constitution of the Polyvinyl Ethers

A closer study of the polymerization products of vinyl ethyl, butyl and chloro-ethyl ethers showed that those obtained by different agents did not differ greatly in physical nature. With the exception of the soft solid formed on heating vinyl chloro-ethyl ether, they are all sticky, pitch-like materials, flowing only very slowly at room temperature but becoming quite fluid on heating above 100° C. They have a faint but characteristic odor when warmed. Solution in chloroform and other solvents takes place very slowly, indicating their high molecular nature. Determination of the molecular weights by freezing-point lowering in benzene showed that the number of molecules of monomer combined in the polymer molecules varied from 18 to 82 in different cases.

It was found impossible to distil any appreciable portion of polyvinyl ethyl ether in a high vacuum. It is likely that the volatile portion observed by Wislicenus (15, p. 113) was simply unchanged monomer.

The densities and indices of refraction of most of these materials were measured. Considerable light is thrown on their internal structure by calculation of the "molecular" refractivities from these data‡. For this purpose it is not necessary that the molecular weight be known. What is actually dealt with is the refractivity of the structural unit or "mer"§.

In the process of polymerization the double bonds originally present in the monomer disappear and are replaced by single bonds between the "mers" in the polymeric chain. If the degree of polymerization be high, we need not consider the question of the disposal of the end valencies, as the differences between the refractivities of the various possible structures will be so small as to be negligible. The theoretical "mer" refractivity is simply the sum of the atomic refractivities of the constituent atoms. The experimental value can be calculated from the density and index of refraction of the polymer by substituting these and the molecular weight of the monomer in the Lorentz-Lorenz formula.

The "mer" refractivities of several polyvinyl ethers are given in Table I. The constants employed in these calculations are listed at the end of this paper. For comparison, the molecular refractivities of the monomers (taken from the preceding paper (3)), are included.

The "mer" refractivities of each of the two pairs of poly-ethers investigated agree satisfactorily with the theoretical. The fact that the polymers obtained

\*See reference to A. Krakau (14, p. 1261).

†Observations on the polymerization of this ester, made in conjunction with Dr. G. S. Whitby of the National Research Laboratories, will be published later.

‡The idea of utilizing the molecular refractivities of high molecular substances to elucidate their constitution is not new. The molecular refractivity of rubber was used many years ago by Gladstone and Hibbert (6, p. 680) and since then in this laboratory (9) to penetrate the structure of the rubber molecule.

§This convenient term has been introduced by Carothers (2, p. 2552).

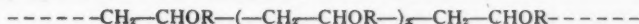
TABLE I  
 "MER" REFRACTIVITIES OF THE POLYVINYL ETHERS

Compound	Found	Theoretical*	Monomer (found)
Polyvinyl ethyl ether (by heat)	20.14	20.11	21.89
(by I)	20.38		
Polyvinyl <i>n</i> -butyl ether (by I)	29.54	29.35	30.94
(by light)	29.23		

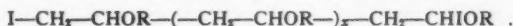
\* Calculated from the atomic refractivities given by v. Auwers and Eisenlohr (5, p. 605).

by different methods vary somewhat in their densities and indices of refraction would not allow us to expect a more exact agreement. This is sufficiently close, however, to show very distinctly that in each polymerization the olefinic linkage has disappeared and has been replaced by two normal, unit bonds.

As polyvinyl ethyl ether gives oxalic acid on oxidation, it may be assumed that it and its analogues possess the regular structure:



Here, as in the case of most other high polymers, it is not easy to decide between an "open" or "ring" formula. In view of recent work on the polyoxymethylenes (11, p. 157), it might be considered that the iodine "polymers" are constituted entirely as the iodides:



It is interesting to note that Wislicenus (15, p. 113) long ago suggested that at least a portion of the "polymer" is made up of such a type of compound. This eminent worker further anticipated later views on the structure of macropolymeric bodies by his suggestion that the iodine is combined in a mixture of a series of "polymer-homologous"\* compounds. The rest of the material he represented as a similar series of large rings formed by the separation of the iodine from the intermediately formed di-iodides. He did not decide between a regular or irregular arrangement of the structural units.

The di-iodide may possibly constitute an intermediate stage in the formation of the true polymer, but it cannot under ordinary conditions form more than a small proportion of the final product. The iodine polymer has an (average) order of polymerization of 82. Utilizing this fact, calculation shows that, when 0.1% of the iodine has been added, only 4.6% of the material can be present as a di-iodide.

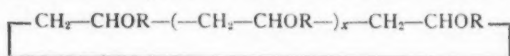
The bromine absorption of the polymers is very small but nevertheless measurable. This fact might be taken to prove the existence of an open-chain structure with an ethenoid linkage at one extremity, *viz.*:



\* To employ an expression for this type of homology more recently suggested by Staudinger (10, p. 3025).

If the polymers possess this formula, the amount of bromine taken up should enable the number of "mers" per macromolecule to be reckoned. When this is done, the values obtained do not show the slightest connection with the orders of polymerization found by cryoscopic measurements. Hence the bromine absorption cannot be adduced in support of either this "open-chain" formula or that with free end valencies.

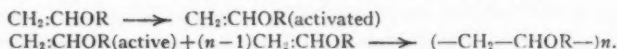
It is very likely that the polymers have actually a "closed-ring" structure:



The slight degree of unsaturation found is probably due to the separation of alcohol under the influence of the strong heating to which the materials are subjected during their preparation or purification. The analytical values obtained from all of the polymers are actually high in carbon and low in hydrogen, corresponding to such a loss.

### Mechanism of the Polymerization of the Vinyl Ethers

In a later paper will be presented grounds for the assumption that, as in other typical polymerizations leading to molecules of considerable size, the reaction is to be considered as a "chain" reaction of the following type:



The first step, consisting in the formation of the "active" molecule, is believed to be unimolecular and to take place at a (comparatively slow) speed which determines the rate of the process as observed. The second step, wherein the formation of the polymeric molecule actually occurs, is completed at an exceedingly great rate. The writer considers it likely that, in the iodine polymerization, the "trigger" molecule is an addition compound with *one* atom of iodine and one free bond, *viz.*,  $\text{ROCHI—CH}_2\text{—}$ .

The course of the polymerization of the vinyl alkyl ethers under the influence of iodine is so easily controllable that it offers a tempting field for the study of the reaction velocities and, hence, of the mechanism of polymerization. The reaction seems to be free from autocatalysis and, from the above assumptions, should be (quasi) unimolecular.

### Experimental

#### *Polymerization of the Vinyl Ethers by Iodine*

The rates of polymerization of the vinyl ethers were determined by adding 1 cc. of chloroform solution, containing 2 gm. of iodine per 100 cc., to 10-gm. quantities of the ethers. The liquids were allowed to stand at room temperature for the period of time noted in each instance. The extent of the change was determined by weighing the residue obtained after subjecting the material to reduced pressure, first at room temperature and then at 200–250°C., for several hours. The results of these measurements are shown in Table II.

Owing to the scarcity of material, no further work was done on vinyl methyl ether beyond the establishment of its sensitivity to iodine. When iodine is

TABLE II  
 POLYMERIZATION OF VINYL ETHERS BY 0.2% IODINE

Ether	Time	Polymer formed, %
Vinyl ethyl ether	6 hr.	88.3
Vinyl ethyl ether	24 hr.	100.0 (approx.)
Vinyl <i>n</i> -butyl ether	24 hr.	100.0 (approx.)
Vinyl $\beta$ -chloro-ethyl ether	6 days	27.7
Vinyl phenyl ether	6 days	2.4 (polymer ?)

added to divinyl ether, the characteristic reaction does not take place, but the halogen is slowly replaced by a white, insoluble solid. This change was not further studied but it is probable that the body is an iodide of divinyl ether.

*Attempt to distil polyvinyl ethyl ether.* A sample of vinyl ethyl ether was polymerized by the addition of  $\frac{1}{1000}$  part of iodine in chloroform solution. After three days, low-boiling compounds were removed by steam distillation. A distillate of the chloroform with a trace of unchanged vinyl ether was obtained. The material was then subjected to the action of superheated steam at 200° C. for several hours. Only a very thin film of an oily liquid could be observed on the surface of the water distillate. On heating the polymer in a distilling flask at a pressure below 0.1 mm. and at a slowly increasing temperature, eventually at 280° C., a mere trace of "balsamous" substance was observed in the receiver.

On heating, the originally amber-colored material becomes black owing to the liberation of free iodine. Continued heating in a high vacuum eliminates the halogen and gives a light-colored material.

*Purification and Examination of the Iodine Polymers*

The polyvinyl ethers obtained with 0.2% iodine were freed from low-boiling impurities as well as most, if not all, of their iodine content by long heating *in vacuo* and retaining over paraffin wax under reduced pressure for several weeks. The densities were determined by a flotation method using small drops of the material, usually in a methanol-water mixture. The suspending medium was freed from dissolved air and the average of a large number of determinations taken. The values are considered to be accurate to one unit in the third place of decimals. The refractive indices could be measured directly on an Abbé refractometer owing to the partial fluidity of the polymers. The constants obtained are shown in Table VI.

*Polyvinyl ethyl ether.* This compound, formed by the agency of iodine, has been analyzed by Wislicenus (15, p. 113) and shown to be (not considering the iodine content) a true polymer. Molecular weight measurements by freezing-point lowering in benzene gave: 5829, 5935.

The bromine absorption was determined with the usual precautions using a *N*/4 solution of bromine in carbon tetrachloride. Bromine solution was added to a weighed quantity of the polymer dissolved in chloroform until a light brown tinge of free bromine was apparent. The containing flask was then stoppered and placed aside for eight hours, when potassium iodide solution

was added and the iodine liberated titrated with standard thiosulphate solution. Potassium iodate solution was then added to determine if any formation of hydrogen bromide (substitution) had taken place, but none could be detected: 0.1850 gm. of polymer absorbed 0.64 cc. of bromine solution. Theoretically, for one double bond per "mer", 20.6 cc. of solution would be needed.

The polymer readily goes into solution on warming with fuming nitric acid. After neutralization, addition of calcium chloride solution gives a voluminous white precipitate which qualitative tests show to be the oxalate.

*Polyvinyl butyl ether.* Analysis gave: Calcd. for  $(C_8H_{12}O)_x$ : C, 71.93; H, 12.09%. Found: C, 71.72; H, 11.91%. Molecular weight, cryoscopic in benzene: 3944, 4025. Bromine absorption: 0.2551 gm. polymer absorbed 0.19 cc. bromine solution ( $N/4$ ). Theoretically for one double bond per "mer", 18.8 cc. would be needed.

*Polyvinyl  $\beta$ -chloro-ethyl ether.* Analysis for chlorine by the method of Piria and Schiff: Calcd. for  $(C_4H_7OCl)_x$ : Cl, 33.3%. Found, 33.0%. The density was determined only roughly, using an aqueous calcium chloride solution as flotation liquid.

#### *Action of Heat on the Vinyl Ethers*

The rates of thermo-polymerization, at 130° C., of the vinyl ethers studied are listed in Table III.

TABLE III  
RATES OF THERMO-POLYMERIZATION OF VINYL ETHERS

Ether	Time, days	Polymer formed, %
Vinyl ethyl ether	60	46.5
Vinyl <i>n</i> -butyl ether	60	26.0
Vinyl chloro-ethyl ether	3	100.0 (approx.)
Vinyl phenyl ether	90	1.6 (polymer ?)

*The vinyl  $\beta$ -chloro-ethyl ether heat product.* This is a soft, black solid insoluble in alcohol and chloroform even after long standing with these solvents. Beyond the determination of its density it was not further studied.

*Vinyl ethyl ether heat product.* On heating to 220° C., the sample gave a liquid which, on redistillation, boiled over the range 60–100° C. It did not contain more than a trace of vinyl ethyl ether but seemed to be composed largely of paraldehyde, as it had the characteristic odor and peculiar water-solubility (less soluble in hot water than in cold) of this compound. On retaining for a month *in vacuo* it lost weight. The composition was as follows: (1) liquid, 60–100° C. (43.5%); (2) loss of weight *in vacuo* (10%); (3) residue (polymer).

The residue was examined as follows: Analysis: Calcd. for  $(C_4H_8O)_x$ : C, 66.61; H, 11.19%. Found: C, 67.38, 67.44; H, 10.48, 10.25%. Molecular weight, cryoscopic in benzene: 1281, 1261.

*Vinyl butyl ether product.* Distillation of the sample gave the following results: (1) liquid; b.p., 93–120° C. (24%); (2) liquid; b.p., 120–180° C. (50%);



(3) residue (polymer). The first fraction reacts violently with iodine and is thus unchanged ether. The nature of the second fraction could not be ascertained. The residue was examined as follows: Analysis: Calcd. for  $(C_6H_{12}O)_x$ : C, 71.93; H, 12.09%. Found: C, 72.13, 72.04; H, 11.23, 11.19%.

*Vinyl phenyl ether.* After heating, came over almost completely at 155–157° C., indicating little or no change. A very small amount of an oily residue, insoluble in sodium hydroxide solution (and which, therefore, could not be phenol), was left in the flask. The material was not analyzed and whether or not it is a true polymer is doubtful.

#### *Photo-polymerization of the Vinyl Ethers*

*Action of quartz lamp.* Samples of vinyl butyl, chloro-ethyl, and phenyl ethers were exposed for seven days to the radiation from a quartz mercury-vapor lamp (110 volts, 3.5 amp.) in  $\frac{3}{4}$ -in. tubes at a distance of 3 in. from the burner. Both the chloro-ethyl and phenyl ethers gave thin coatings of yellow, gelatinous solids on the walls of the tubes. The bulk of the product from the chloro-ether was, however, a material resembling the iodine polymer. The constants of this body were not determined owing to its lack of homogeneity. The phenyl ether showed no further change beyond the formation of the trace of insoluble material. The results obtained are listed in Table IV.

TABLE IV  
EFFECT ON VINYL ETHERS OF IRRADIATION WITH A QUARTZ MERCURY-VAPOR LAMP (7 DAYS)

Ether Polymer formed, %	Vinyl <i>n</i> -butyl 61	Vinyl chloro-ethyl 66	Vinyl phenyl Trace (polymer ?)
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The photo-polymer of vinyl butyl ether was purified by retaining *in vacuo* over paraffin wax for several weeks. Bromine absorption: 0.4672 gm. polymer absorbed 0.22 cc. of bromine solution (*N*/4). Theoretically, for one double bond per "mer", 37.4 cc. would be needed.

*Action of sunlight.* Samples of all of the ethers prepared, including divinyl ether, were exposed in quartz as well as glass tubes, on a sunny window-ledge for periods extending from a month to a year. In no case was any observable change found on distillation.

#### *Order of Polymerization and Bromine-absorption Measurements*

The orders of polymerization calculated from the molecular weights, and the corresponding values calculated from the measured bromine absorption, on the assumption of an open-chain formula are shown in Table V.

#### *Action of Other Agents on the Vinyl Ethers*

Stannic chloride and antimony pentachloride, added in the proportion of one drop of 20% solution in chloroform to several cc. of the ethers, gave violent almost explosive, reactions. Resinous products are formed as with iodine, but these are marred by an intense black discoloration.

Samples of vinyl ethyl, butyl, and phenyl ethers were allowed to stand for several months over sodium wire. On distillation, the boiling points of the

TABLE V  
ORDERS OF POLYMERIZATION OF SOME POLYMERS OF VINYL ETHERS

	Polyvinyl ethyl ether		Polyvinyl butyl ether	
	By iodine	By heat	By iodine	By heat
Order of polymerization calculated from cryoscopic measurements	82	18	40	—
Number of "mers" per double bond calculated from bromine absorption	32	—	100	170

liquids were found to be unchanged and no residues were left. A sample of vinyl butyl ether treated with several crystals of metaphosphoric acid became discolored but gave no appreciable amount of polymer on long standing.

TABLE VI  
DENSITIES AND INDICES OF REFRACTION OF THE POLYVINYL ETHERS

	Density	Refractive index
Polyvinyl ethyl ether		
Iodine polymer	$D_4^{20}$ : .975	$n_D^{20}$ : 1.4624
Heat polymer	$D_4^{20}$ : 1.010	$n_D^{20}$ : 1.4769
Polyvinyl <i>n</i> -butyl ether		
Iodine polymer	$D_4^{20}$ : .933	$n_D^{20}$ : 1.4629
Heat polymer	—	$n_D^{20}$ : 1.4748
Light polymer	$D_4^{25}$ : .947	$n_D^{25}$ : 1.4652
Polyvinyl $\beta$ -chloro-ethyl ether		
Iodine polymer	$D_4^{20}$ : 1.25	$n_D^{20}$ : 1.4967
Heat polymer	$D_4^{20}$ : 1.210	Opaque

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## STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

### XLII. THE SYNTHESIS OF CELLULOSE *o*-CHLOROBENZYL ETHERS AND MECHANISM OF THEIR FORMATION<sup>1</sup>

BY R. H. BALL<sup>2</sup> AND HAROLD HIBBERT<sup>3</sup>

#### Abstract

A method has been developed for the study of the specific effect of the factors involved in the synthesis of cellulose *o*-chlorobenzyl ethers, and applied to an investigation of the most important of the reaction variables. The usefulness of the data thus obtained in studying the mechanism of the reaction, and in supplying new information on the chemical properties of soda cellulose, has been pointed out. The latter application of the data has been made possible by the development of a method for the quantitative separation of the cellulose mono- and lower ethers from the higher cellulose ethers.

It has been shown that in the reaction between soda cellulose and *o*-chlorobenzyl chloride, the extent to which ether formation occurs is influenced to a marked degree by the temperature of the reaction and the alkali concentration used in the preparation of the soda cellulose. Increase in either, or both, of these factors results in increased ether formation, such increase taking place, however, in a somewhat complex manner. It has been found possible to interpret the irregularities in the effect of these two variables, namely, temperature and alkali concentration, in accordance with a kinetic conception of the reaction, which assumes the existence of an equilibrium mixture of mono-, sesqui-, and di-sodium celluloses in the soda cellulose employed. Evidence has been presented for the definite existence of a sesqui-*o*-chlorobenzyl ether of cellulose,  $C_{12}H_{17}O_{10}$  ( $C_7H_4Cl$ )<sub>2</sub>.

The effect of temperature on *o*-chlorobenzyl ether formation has been studied at one definite alkali concentration (20 gm. of sodium hydroxide per 100 cc.), and the effect of concentration at one definite temperature (95° C.). Based on the results obtained, a final experiment was performed, which showed that the influence of each variable is specific, and that these factors can be altered in such a manner as to lead, qualitatively at least, to the synthesis of ethers of well-defined structure.

The limited experimental data obtained on the influence of the duration of "steeping" and "aging" of the soda cellulose appear to indicate that during these processes a combination of oxidation and depolymerization changes occur, leading to an increase in the solubility of the cellulose derivatives formed.

An initial equilibrium apparently exists between the primary sodium cellulose and the sesqui sodium cellulose, the formation of the latter being favored both by increasing alkali concentration and higher temperature. The shifting of this equilibrium, with increase in the reaction temperature and concentration of the alkaline steeping liquor, in the direction of the sesqui sodium cellulose is followed immediately by the establishment of a second equilibrium between the latter and disodium cellulose, as shown by the fact that the sesqui cellulose *o*-chlorobenzyl ether can be obtained free from the cellulose di-ether only over a very limited range of temperature and concentration.\*

#### Introduction

The present data regarding the synthesis and structure of the ethers of cellulose exhibit many peculiarities which do not afford a simple interpretation based on the generally accepted theory that cellulose is a supermolecular

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<sup>2</sup> Postgraduate student at McGill University.

<sup>3</sup> Professor of Industrial and Cellulose Chemistry, McGill University.

\* An investigation of this equilibrium at various temperatures is to be carried out. (H.H.)

product made up of building units containing hydroxyl groups in the ratio of one primary to two secondary groups. Instances are available in which the substitution of one, of two, or of all three of the cellulose hydroxyl groups (per  $C_6$  unit) appears to be the limit of the etherification, the extent of the reaction depending presumably on the nature of the etherifying agent and on the reaction conditions employed. Neither of these two factors has received any systematic study. In this paper the authors have initiated such a study by an investigation of the effect of reaction conditions on the yield and nature of the ethers formed by the interaction of soda cellulose and *o*-chlorobenzyl chloride.

The literature provides little explanation of the peculiarities of cellulose ether formation, as shown by the following examples. The dialkyl sulphates and aqueous alkali, in a multiple-stage reaction, have been found to substitute all three of the cellulose hydroxyl groups (3, 4, 9, 10). On the other hand, triphenyl methyl chloride, with pyridine as the condensing agent, is able to react with only the primary hydroxyl group, forming the mono cellulose ether exclusively (8). The interaction of ethyl chloride with soda cellulose was found to yield cellulose triethyl ether (1), while allyl bromide and soda cellulose react to form the diallyl ether of cellulose (21, 24). The reaction of cellulose with chloracetic acid and sodium hydroxide solution was found by Sakurada (22) to yield only the mono cellulose ether, whereas Chowdhury (2), by using more concentrated alkaline solution, succeeded in obtaining the tri-ether. In the interaction of benzyl chloride with soda cellulose several ethers are stated to be formed. Gomberg and Buchler (7) presented evidence for the existence of hemi-, sesqui-, and di-benzyl ethers of cellulose, but their method of purification has been shown to be unsatisfactory by Nakashima (12), who demonstrated that the actual products of the reaction were cellulose mono- and di-benzyl ethers, the latter representing the limit of the substitution, a result also supported by the work of Okada (14).

A careful review of the methods and conditions used in the investigations quoted above provides no general explanation of the limitations in reactivity shown by the hydroxyl groups of cellulose in ether formation. In only two cases is a ready explanation fairly obvious. For example, in the reaction with triphenyl methyl chloride, the well-known specificity of this reactant for primary hydroxyl groups accounts for the result obtained, while with chloracetic acid the concentration of sodium hydroxide solution appears to be the controlling factor. The other examples which have been cited afford no general theory explanatory of their peculiarities, especially since most of the reaction conditions have been varied so widely as to make it impossible to draw conclusions as to their effect on the extent of etherification.

The work on benzyl ethers of cellulose quoted above merits some further attention, as it indicates the possible effect of alkali concentration on the degree of substitution obtained. Thus, while Gomberg and Buchler were undoubtedly incorrect in the characterization of their benzyl ethers, they claim to have obtained a cellulose hemi-benzyl ether from a one-stage reaction using 20%

sodium hydroxide solution, a sesqui-benzyl ether from a one-stage reaction using 30% sodium hydroxide solution, and a di-benzyl ether from a two-stage reaction using 30% sodium hydroxide solution. Nakashima claimed a quantitative yield of the di-benzyl ether by using 40 to 50% sodium hydroxide solution, and Okada likewise used 50% sodium hydroxide solution in preparing the di-ether. Thus, by correlating the data of these investigations, a general relation between alkali concentration and degree of etherification appears probable.

Other ethers of cellulose, still more closely related to those which are the subject of this paper, have been prepared by Niethammer and König (13) by the action of *p*-chlorobenzyl chloride on cellulose. No pure ethers of cellulose were isolated by these workers, and the degree of etherification obtained was usually less than that of the mono-ether, in spite of purification with cuprammonium hydroxide solution. Their research appears to have been undertaken for the purpose of studying the effect of the reaction conditions on the nature of the products formed, but so many conditions were varied, and in such a haphazard manner, that it is impossible to draw any conclusions from their work.

From this brief review it appears that the limited ability of the individual hydroxyl groups of cellulose to form ethers is controlled in some way by the reaction conditions. Thus there is evidence that the concentration of the alkaline solution used to prepare the soda cellulose may have an important bearing on this point. On the other hand, other reaction conditions, such as temperature, molecular proportions, "aging" of the soda cellulose, use of solvents, etc., may have an equally important influence on the extent to which cellulose ethers are formed. The effect of these variables has received even less attention than that of alkali concentration. The present investigation was undertaken to study systematically the effect of the reaction variables on the yield and nature of the cellulose ethers formed from the interaction of soda cellulose and *o*-chlorobenzyl chloride, in the hope that the data obtained would have some value as such, and would also throw some light on the chemical nature of soda cellulose.

The structure of soda cellulose has been the subject of a great deal of research. It has long been known that cellulose, when immersed in aqueous alkaline solution, absorbs alkali in such a manner as to establish an equilibrium between that taken up by the fibre and that remaining in the solution. Although very little is known about the effect of temperature on this equilibrium, the effect of alkali concentration has received considerable attention, and has given rise to various interpretations based on the chemical structure of soda cellulose.

There is general agreement by most workers regarding the shape of the curve representing the absorption of alkali by cellulose. When cellulose is immersed in an aqueous sodium hydroxide solution, the concentration of alkali in the supernatant liquid shows a considerable decrease as a result of the alkali taken up by the cellulose. This might be attributed to adsorption if the amount of alkali associated with the cellulose did not show such a definite and irregular

relation to the initial concentration of the alkaline solution. Thus the amount of alkali taken up by the cellulose increases more or less steadily as the alkali concentration is increased to 16 gm. of sodium hydroxide per 100 cc. of solution, when no further absorption is observed until a concentration of 24 gm. per 100 cc. is exceeded. This irregularity in the absorption curve has generally been attributed to the formation of a definite chemical compound between cellulose and sodium hydroxide.

The quantitative study of the nature of this compound between cellulose and sodium hydroxide presents certain difficulties, and there has been considerable controversy as to whether it is a hemisodium cellulosate or a monosodium cellulosate. Of the two older methods for studying this problem, the "indirect" method was thoroughly investigated by Rassow (17), and the "direct" method by Heuser and Niethammer (11) and also by Rassow (17). The results of both of these methods point to the existence of a compound containing two glucose units of cellulose combined with one molecule of sodium hydroxide. Both methods, however, are open to serious criticism, as pointed out by Schwartzkopf (23), and too much confidence should not be placed in these results. A new method of differentiating between free and combined alkali has recently been developed by Percival, Cuthbertson and Hibbert (15). The data of these workers point very definitely to the fact that the break in the cellulose-sodium hydroxide absorption curve represents the formation of the compound  $(C_6H_{10}O_5)NaOH$ , containing 25.3 gm. of sodium hydroxide per 100 gm. of cellulose, and not  $(C_6H_{10}O_5)_2NaOH$ .

A clear picture of the significance of the cellulose-sodium hydroxide absorption curve is important for the interpretation of the data presented in this paper. The first portion of the curve represents the equilibrium between monosodium cellulosate and aqueous sodium hydroxide, the equilibrium favoring the former as the concentration of the latter is increased, until at 16 gm. of sodium hydroxide per 100 cc. the cellulose has been completely transformed into monosodium cellulosate. The break in the curve at this point further indicates that one hydroxyl group in each glucose unit of the cellulose is much more reactive towards alkali than the other two, since this hydroxyl group shows complete combination at a concentration considerably below that required for the other two to enter into reaction. This interval between the completion of the one reaction and the commencement of the other is responsible for the horizontal portion of the curve. The assumption that the first hydroxyl group to combine with sodium hydroxide is the primary one is based on analogy with the action of sodium ethylate on glycerol, by which  $\alpha$ -monosodium glyceroxide is obtained exclusively (6). Furthermore, the continued rise in the curve after the concentration of 24 gm. of sodium hydroxide per 100 cc. has been reached indicates that the secondary hydroxyl groups enter into reaction with the sodium hydroxide above this point. Thus it is possible to draw a fairly clear picture of the effect of alkaline concentration on the reaction between cellulose and sodium hydroxide.

In the brief review of cellulose ether formation, it was pointed out that the specific ability of the individual cellulose hydroxyl groups to form ethers appeared to be controlled in some way by the reaction conditions. Since the reactants with which this study is concerned consist of *o*-chlorobenzyl chloride and the various sodium celluloses comprising "soda cellulose", the effect of the reaction conditions must be due chiefly to their influence on the amount and chemical nature of these sodium celluloses. Unfortunately it is impossible to apply the present information concerning soda cellulose directly to its reaction with alkyl halides, since this reaction usually requires a much higher temperature than has been used in the above investigations on soda cellulose (20 to 25° C.). Moreover, no studies have been carried out on the effect of temperature on the absorption of sodium hydroxide by cellulose. However, it seems probable that there will be some similar difference in the reactivity of the primary and secondary hydroxyl groups at higher temperatures, and that this difference will make itself evident in the cellulose ether reaction products.

### Discussion of Results

The experimental results show the effect of time, temperature, concentration of sodium hydroxide solution, and time of steeping, on the products of the reaction between soda cellulose and *o*-chlorobenzyl chloride, and have been interpreted on the basis of the equilibrium between the different sodium celluloses which was postulated in the introduction. The general trend of these reaction variables has been determined, and sufficient experimental data obtained to enable conclusions to be drawn as to the mechanism of the reaction, and to indicate the possibilities of obtaining information from a further study of this subject.

The chlorine content of the cellulose *o*-chlorobenzyl ethers was used to determine the extent of ether formation. To facilitate the discussion of the subject, the calculated percentage of chlorine of each of the possible cellulose *o*-chlorobenzyl ethers is given below:

Cellulose hemi- <i>o</i> -chlorobenzyl ether $C_{12}H_{19}O_{10}(C_7H_6Cl)$	Contains one <i>o</i> -chlorobenzyl ether unit per two anhydro glucose units. (Insoluble)*	7.90% Cl
Cellulose mono- <i>o</i> -chlorobenzyl ether $C_{12}H_{18}O_{10}(C_7H_6Cl)_2$ or $C_6H_5O_5(C_7H_6Cl)$	Contains one <i>o</i> -chlorobenzyl ether unit per one anhydro glucose unit. (Insoluble)*	12.37% Cl
Cellulose sesqui- <i>o</i> -chlorobenzyl ether $C_{12}H_{17}O_{10}(C_7H_6Cl)_3$	Contains three <i>o</i> -chlorobenzyl ether units per two anhydro glucose units. (Soluble)*	15.25% Cl
Cellulose di- <i>o</i> -chlorobenzyl ether $C_{12}H_{16}O_{10}(C_7H_6Cl)_4$ or $C_6H_5O_5(C_7H_6Cl)_2$	Contains two <i>o</i> -chlorobenzyl ether units per one anhydro glucose unit. (Soluble)*	17.25% Cl
Cellulose tri- <i>o</i> -chlorobenzyl ether $C_6H_7O_5(C_7H_6Cl)_3$	Contains three <i>o</i> -chlorobenzyl ether units per one anhydro glucose unit. (Soluble)*	19.85% Cl

\*Chloroform employed as solvent.



## SOLUBILITY

The solubility of the reaction products was an important factor in determining the type of ether obtained from each reaction. Throughout all these experiments, with the exception of two in which the soda cellulose was aged for 12 and 48 hr. respectively, the cellulose *o*-chlorobenzyl ethers were characterized sharply by their behavior towards chloroform. Treatment with this solvent permitted of a sharp division into two different types: (a) those containing less than 12.35% chlorine, which were insoluble in chloroform, and (b) those containing more than 15.26% chlorine, soluble in this solvent. With the two exceptions noted above, no ethers were found having a chlorine content between 12.35 and 15.26%. It is significant that these values correspond very closely with those calculated for the mono-ether (12.37% Cl) and the sesqui-ether (15.25% Cl) respectively. We can therefore say that ethers up to and including the mono-ether are insoluble in chloroform, while the sesqui and higher ethers are soluble. Moreover, both in the temperature series of experiments (Fig. 2, curve 4), and in the alkali concentration series (Fig. 3, curve 3), the sesqui-*o*-chlorobenzyl ether was formed under the minimum conditions permitting the formation of a soluble ether. Since the mono-ether is insoluble in chloroform, as shown by repeated extraction, and by the absence of ethers having a chlorine content between 12.35 and 15.26%, the individuality of this sesqui-ether must be assumed in order to account for the isolation of a product containing 15.26% chlorine.

RELATION BETWEEN REACTION CONDITIONS AND YIELD AND NATURE OF THE CELLULOSE *o*-CHLOROBENZYL ETHERS FORMED(a) *Effect of Excess Alkaline Solution*

Much greater etherification was effected when the excess of the sodium hydroxide steeping solution was removed from the soda cellulose before its reaction with *o*-chlorobenzyl chloride.

(b) *Effect of Inert Diluents*

The presence of inert diluents, such as benzol or toluol, was found to hinder the reaction between soda cellulose and *o*-chlorobenzyl chloride.

(c) *Effect of Reaction Time*

This series of experiments, the results of which are plotted in Fig. 1, was

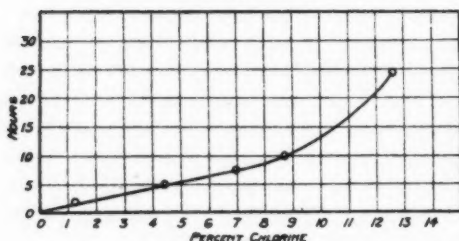


FIG. 1. Time curve. Alkali concentration, 20 gm. of sodium hydroxide per 100 cc. Temperature, 90°C.

carried out to determine a reasonable reaction time, and to test the reliability of the experimental procedure. The method of purifying the reaction products of this series resulted in a complete recovery of the ethers, both soluble and insoluble, but not in a separation into soluble and insoluble fractions.

Since a large number of experiments were to be performed, it was



necessary to arrive at a compromise between a reasonable degree of etherification and time of reaction. The times recorded in the literature vary from 2 (5) to 100 hr. (13). As the time curve found showed an almost linear relation between percentage of chlorine and time up to nine hours, and the reaction began to slow up beyond that point, ten hours was selected as a reasonable duration for the reaction.

The reliability of the methods used in carrying out these reactions and the purifying of the products is shown by the fact that the chlorine values in this series fall on a smooth curve. Each point on the curve represents a different experiment, carried out in exactly the same way as the other experiments in the series, except for an alteration in the length of time the reaction mixture was heated.

(d) *Effect of Reaction Temperature (Fig. 2)*

The results of the series of experiments dealing with the effect of temperature variation on the reaction between soda cellulose and *o*-chlorobenzyl chloride have been plotted in Fig. 2, curves Nos. 1 to 5. From these curves it can be seen that the extent of ether formation, as indicated by the yield and chlorine content of the products, increases in a complex way as the temperature is raised.

In Fig. 2, curve No. 1 has been plotted from a preliminary temperature study, and curve No. 2 from the final work on temperature. Reference to the Experimental Part will show that the series of experiments plotted in curve No. 1 (excluding the dotted portion) is similar to that summarized in curve No. 2, except that the reaction time was seven hours in the former series, and ten hours in the latter. Comparison between these two curves shows that there is the expected increase in the rate of ether formation with rise in temperature, but that the rate of this increase is suddenly diminished at 90 to 95° C. Since this slowing up occurs at the same temperature but at different percentages of chlorine in the two curves, it must be a phenomenon associated with that particular temperature, and not with the formation to completion of any specific ether.

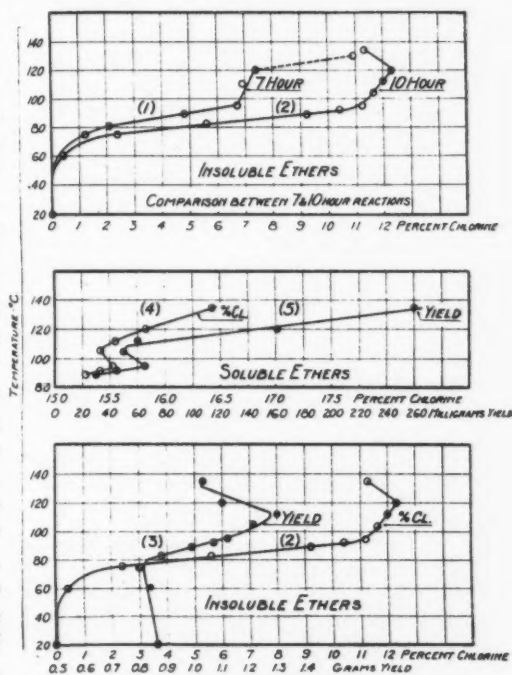


FIG. 2. Temperature curve. Alkali concentration, 19.9 gm. of sodium hydroxide per 100 cc. Time (except curve No. 1), 10 hr.

This is the only important point arising from a comparison of curves Nos. 1 and 2.

With this point in mind, the following conclusions regarding the effect of temperature on *insoluble* ether formation may be drawn from the shape of curves Nos. 2 and 3. As the reaction temperature is raised the rate of formation of the insoluble *o*-chlorobenzyl ethers, as measured by yield and chlorine content, increases until a temperature of 90 to 95° C. is reached. At this point the rate of increase slows up quite sharply, the insoluble ether formation finally passing through a maximum at 110 to 120° C. At the maximum point the insoluble product analyzed 12.35% chlorine, corresponding to cellulose mono-*o*-chlorobenzyl ether.

Turning to the effect of temperature on *soluble* ether formation, as presented in curves Nos. 4 and 5, it is seen that the soluble ethers make their appearance at about 90° C. with the formation of the cellulose sesqui-*o*-chlorobenzyl ether, and increase both in yield and in chlorine value as the temperature is raised, this increase taking place most rapidly after 110° C. has been exceeded. Thus the soluble ethers are first obtained at the temperature at which insoluble ether formation begins to slow up, and start to form rapidly at the temperature at which insoluble ether formation reaches its maximum. The most highly substituted soluble ether obtained in this series contained 16.42% Cl, considerably below that calculated for the di-ether.

(e) Effect of Alkali Concentration (Fig. 3)

The results obtained from the study of the relation between the concentration of the alkaline steeping solution and cellulose ether formation have been

plotted in Fig. 3. Here it is seen that there is an increase in ether formation as the concentration of the steeping solution is raised. The relations involved, however, are not simple. In this series of experiments the reactions were carried out at 95° C. for ten hours.

Curves Nos. 1 and 2 of this series show the effect of alkali concentration on the formation of the *insoluble* cellulose *o*-chlorobenzyl ethers. From these curves it is seen that, as the concentration of sodium hydroxide is increased to 25 gm. per 100 cc., the formation of the insoluble ethers increases to a maximum, giving

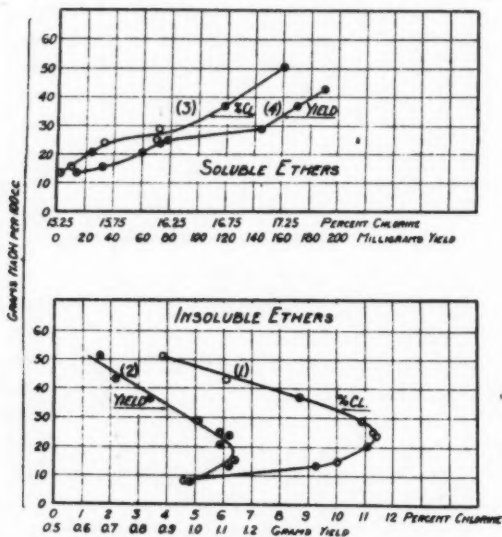


FIG. 3. Alkali concentration curve. Temperature, 95° C. Time, 10 hr.

a product containing 11.38% Cl. Above this concentration both the yield and chlorine content of the insoluble ethers decrease rapidly.

Curves Nos. 3 and 4 of this series show the relation between alkali concentration and formation of *soluble* cellulose *o*-chlorobenzyl ethers. Soluble ethers begin to form at a sodium hydroxide concentration of 13.6 gm. per 100 cc., with a small yield of a product analyzing 15.27% Cl, corresponding to cellulose sesqui-*o*-chlorobenzyl ether. As the alkali concentration is raised, both the yield and chlorine content of the soluble ethers increase until a product corresponding to the di-ether is obtained at a concentration of 50 gm. of sodium hydroxide per 100 cc.

(f) *Effect of Altering the Time of Steeping*

This series of experiments is not extensive enough to require graphic presentation. Table V in the Experimental Part demonstrates that the yield of, and percentage of chlorine in, the soluble and insoluble ethers of cellulose decrease as the length of time of steeping is increased, maximum ether formation taking place with the shortest steeping time. This decrease is quite negligible in the case of the actual yield and chlorine content of the *insoluble* ethers, but is sufficient in considering the percentage of chlorine in the *soluble* ethers to call for further discussion, especially since two of the values obtained fall within the region 12.37 to 15.25% Cl, in which no products had previously been found. Thus the soluble *o*-chlorobenzyl ethers of cellulose resulting from the reactions using soda cellulose which had been steeped for 12 and 48 hr. respectively contained in both cases 14.14% Cl.

The phenomena associated with the aging of soda cellulose have been explained on the basis of oxidation, or depolymerization, or both (19, 25, 26). Either one of these processes would result in an increased solubility of the cellulose reaction product, and might conceivably render a part of the lower "insoluble" cellulose ethers soluble in chloroform. A decrease in the chlorine content of the soluble ethers, due to contamination by lower ethers rendered soluble through "aging" the soda cellulose, is, therefore, to be expected. This hypothesis is confirmed by the series of experiments under discussion, in which the decrease in the chlorine content of the soluble ethers is the only striking fact.

The formation from "aged" soda cellulose of a cellulose *o*-chlorobenzyl ether containing 14.14% Cl does not invalidate the arguments which have been presented for the existence of the cellulose sesqui-*o*-chlorobenzyl ether. The evidence for the existence of this ether has been based on two facts:— (a) the very specific percentage of chlorine which is shown by the soluble ether first formed in any series (15.27%); and (b) the insolubility in chloroform of the cellulose mono-*o*-chlorobenzyl ether, as shown by the fact that no *soluble* ethers were found containing less than 15.25% Cl, and no *insoluble* ethers analyzing more than 12.37% Cl. The only exceptions to these latter results are the two products containing 14.14% Cl. Since the peculiar solubility responsible for these products is associated with the changes taking place during long steeping, and this condition did not obtain in the rest of the work,

these two exceptions do not disturb the validity of the arguments presented for the existence of the cellulose sesqui-*o*-chlorobenzyl ether.

(g) *Effect of Altering Reaction Temperature and Alkali Concentration Simultaneously*

The data which have been presented on the effect of temperature and alkali concentration show that a high concentration of sodium hydroxide or a high temperature, individually, favor a high degree of substitution and a high yield of soluble cellulose *o*-chlorobenzyl ether. It therefore seemed probable that increasing the temperature and alkali concentration simultaneously would result in a high yield of highly substituted soluble ether.

This was confirmed in two experiments. In the first, using a reaction temperature of 120° C. and a sodium hydroxide concentration of 50 gm. per 100 cc., the yield of soluble ether from one gram of pulp was 1.02 gm., four times that obtained in any of the other experiments performed, and the chlorine value of 16.85% was within 0.4% of that calculated for the di-ether. Both the yield and percentage of chlorine of the insoluble ether were very low. In the second experiment, using a reaction temperature of 120° C., a longer reaction time (15 hr.), and a sodium hydroxide concentration of 70 gm. per 100 cc., five grams of sulphite pulp yielded 6.6 gm. of soluble ether and only 0.65 gm. of insoluble ether.

MECHANISM OF THE REACTION BETWEEN SODA CELLULOSE AND  
*o*-CHLOROBENZYL CHLORIDE

In interpreting the curves which have been presented in Figs. 2 and 3, one point especially must be kept in mind; namely, that unchanged cellulose has not been removed from the reaction products, and will be present in the fraction which has been called "insoluble ethers". This fraction, therefore, comprises cellulose mono-*o*-chlorobenzyl ether, lower cellulose ethers (if such exist), and unchanged cellulose. Since the reactions were run for a definite period, and not to completion, there will be a certain amount of unchanged cellulose resulting from most of the reactions. This cellulose could have been removed from the insoluble ether fraction by treatment with cuprammonium hydroxide solution, but it was found that four or five successive treatments would be necessary to effect this purification. The large number of experiments to be run made it necessary to omit the cuprammonium hydroxide treatment. Thus both the yield of, and percentage of chlorine in the insoluble ethers will be affected by the amount of unchanged cellulose present.

The most logical interpretation of the data presented in Figs. 2 and 3, and the one which finds greatest substantiation in our present knowledge of soda cellulose, is that based on the equilibrium between sodium hydroxide solution and the different sodium celluloses. The experimental results obtained require the assumption that this equilibrium is influenced both by alkali concentration and by temperature. The former influence has been investigated at 20 to 25° C., but not at the temperatures necessary to form cellulose ethers. The influence of temperature on this equilibrium has not been studied hitherto.

(a) *Influence of Temperature on Soda Cellulose and its Reaction Products*

Consider first the effect of temperature increase on the *insoluble* cellulose ether formation, as presented in Fig. 2, curves Nos. 2 and 3, assuming that higher temperatures cause a shift in the equilibrium from the monosodium cellulosate towards the sesqui and disodium cellulosates. At the alkali concentration used in this series of experiments, namely, 19.9 gm. of sodium hydroxide per 100 cc., the monosodium cellulosate should be formed to completion at the lowest temperature used. As the temperature is raised, the rate of reaction between *o*-chlorobenzyl chloride and monosodium cellulosate will increase, resulting in (a) greater formation of cellulose mono-*o*-chlorobenzyl ether, (b) increase in the ratio of the latter to unchanged cellulose, and (c) a consequent increase in the chlorine content and yield of the insoluble ether fraction. This corresponds with the first portion of curve No. 2. The initial decrease in yield shown in the first portion of curve No. 3 is probably due to increasing solubility of cellulose in sodium hydroxide solution as the temperature is raised, an effect which is overtaken as the cellulose ethers begin to form rapidly. When a temperature of 90 to 95° C. has been reached, a shift in the equilibrium from mono to sesqui and disodium cellulosate commences, resulting in a reduction in the amount of monosodium cellulosate present in the reaction mixture. While this does not immediately cause a decrease in the chlorine content of the *insoluble* ether fraction, because of (a) the continued effect of temperature in increasing reaction velocity, and (b) the diminution in the amount of unchanged cellulose due to its transformation into soluble ethers, it is nevertheless sufficient to reduce the rate of increase of chlorine content which prevailed in the first portion of the curve. Finally, with further increase in temperature to 110 to 120° C., so much of the monosodium cellulosate has changed over to higher sodium cellulosates, and the amount of cellulose mono-ether formed has consequently become so reduced, that the ratio of cellulose mono-*o*-chlorobenzyl ether to cellulose commences to decrease, and the chlorine content of the insoluble ether fraction starts to drop. It should be pointed out that, due to decrease in the amount of unchanged cellulose, caused by its transformation into soluble ethers, the maximum in chlorine content of the insoluble ethers will come at a temperature above the true maximum, and that of the yield curve below the true maximum.

Curves Nos. 4 and 5, depicting *soluble* ether formation, confirm the above interpretation of the influence of temperature on this reaction. Thus the temperature of 90 to 95° C., at which the start of a shift from mono to sesqui and disodium cellulosates was postulated, is associated with the beginning of soluble ether formation. Furthermore, the temperature of 110 to 120° C. corresponds with a very rapid increase in soluble ether formation, supporting the assumption that a far-reaching change towards the higher sodium cellulosates has taken place by the time this temperature is reached, a change which is also responsible for the maximum value of insoluble ether formation.

The interpretation presented above suggests the following picture of the effect of temperature on a soda cellulose prepared from sodium hydroxide



solution containing 19.9 gm. of sodium hydroxide per 100 cc. The soda cellulose consists almost entirely of monosodium cellulosate up to a temperature of 90 to 95° C. At this point the formation of sesquisodium cellulosate, associated almost immediately with some disodium cellulosate, commences, thus reducing the amount of monosodium cellulosate. By the time the temperature has reached 110 to 120° C., this shift in the equilibrium is largely in favor of the higher sodium cellulosates.

*(b) Influence of Alkali Concentration on Soda Cellulose and its Reaction Products*

The interpretation of the curves in Fig. 3 is very similar to that which has just been presented for Fig. 2, except that it is not complicated by the effect of temperature on reaction velocity. The effect of alkali concentration on the sodium hydroxide-sodium cellulosate equilibrium at 20 to 25° C. has already been discussed in the introduction. Some similar relation may be expected at the temperature of 95° C. at which this series of reactions was conducted, although there is no reason to assume that the changes in equilibrium will come at the same concentration or be as clearly defined as at the lower temperature.

In the series of experiments studying alkali concentration, presented in Fig. 3, it is seen that the initial alkali concentration was 8.6 gm. of sodium hydroxide per 100 cc., which is probably below that required to cause complete formation of monosodium cellulosate at the temperature of the reaction. Therefore, as the concentration is increased, the amount of monosodium cellulosate in the reaction mixture will rise, bringing an increase in the chlorine content and yield of the insoluble cellulose ethers. This increase will tend to continue until the alkali concentration is sufficient to form the monosodium cellulosate to completion, unless, due to the temperature used, the higher sodium cellulosates start to form before the primary hydroxyl group has completely reacted. For the same reasons as were given in the discussion of the temperature curves, the formation of the higher sodium cellulosates, increasing as the alkali concentration is raised, will tend to lower first the yield, and then the chlorine content, of the insoluble ethers, resulting in a maximum in both these curves. The fact that the maximum in the percentage of chlorine of the insoluble ethers occurs at an alkaline concentration (23.9 gm. of sodium hydroxide per 100 cc.) above that necessary for soluble ether formation (13.6 gm. per 100 cc.) suggests that at 95°C. the formation of sesqui and disodium cellulosates commences at an alkali concentration below that necessary to cause complete formation of monosodium cellulosate.

From the discussion which has just been presented, it will be seen that the systematic investigation of the variables in the reaction between soda cellulose and an alkyl halide has provided a new angle from which to attack the problem of the chemical nature of soda cellulose, and has thrown some light on the constitution of this highly complex substance.

### Experimental

*(a) Method of Analysis*

Since the chlorine atom in the *o*-chlorobenzyl group is stable to alkali under the conditions of cellulose ether formation, chlorine analysis was used to deter-



mine the degree of etherification of the cellulose *o*-chlorobenzyl ethers. In seeking a rapid and accurate method of chlorine analysis, numerous methods were tried, including the micro-method of Pregl (16, pp. 104-118), a micro-modification of the Carius method, the semi-micro method of Willard and Thompson (27), and the macro-method of Robertson (19, 20). The last three of these all proved reliable, with the Willard and Thompson method exhibiting several advantages over the micro-Carius for work on a small scale.

(b) *Preliminary Experiments*

In some of the work on cellulose ethers recorded in the literature, the excess of alkaline steeping solution was not removed from the soda cellulose before it was brought into reaction with the alkyl chloride, while other workers removed the steeping solution by pressure or suction. The relative merits of these two procedures were tested by two parallel experiments.

*Experiment 1.* One gram of cellulose\* was steeped at room temperature for two hours with 10 cc. of 20% sodium hydroxide solution, 16 gm. of *o*-chlorobenzyl chloride added, and the reaction mixture heated for seven hours at 95° C. The reaction product was removed by filtration and purified by washing with alcohol and ether. Analysis:— Found: Cl, 0.19, 0.74%; mean, 0.43%.

*Experiment 2.* This was a duplicate of Experiment 1, except that the excess of alkaline solution was removed by pressure and suction before adding the *o*-chlorobenzyl chloride. Analysis:— Found: Cl, 6.64, 6.84%; mean, 6.74%. The improvement on removing the excess steeping solution is obvious.

*Experiment 3.* In the literature there are numerous references to the use of an inert solvent in the synthesis of cellulose ethers. The value of this procedure was tested by an experiment which duplicated Experiment 2, except that 15 cc. of toluene was added to the reaction mixture. Analysis:— Found: Cl, 3.13, 2.95%; mean, 3.04%. Comparison of this result with that of Experiment 2 shows that the use of the solvent is detrimental to cellulose ether formation.

*Experiment 4.* This duplicated Experiment 2 in every respect, and was run to see how closely results could be checked. Analysis:— Found: Cl, 6.56, 6.29%; mean, 6.42%.

*Standard procedure.* This work called for several series of experiments, to be run under conditions as nearly comparable as possible. As a result of the above experiments, the following was set up as a standard reaction procedure to be used throughout the work. One gram of cellulose was steeped in 10 cc. of sodium hydroxide solution of known concentration for a specified time in a 125-cc. Erlenmeyer flask closed with a rubber stopper. The wet soda cellulose was transferred to a sintered glass filter and placed under suction for two minutes, during which it was pressed down on the filter with a glass pestle. The same filter and water pump were used throughout the work. Suction was continued for only two minutes to minimize the formation of sodium

\*The cellulose used in this investigation was highly purified alpha sulphite pulp provided by the Brown Company, Berlin, New Hampshire, to whom the authors wish to express their thanks for the gift of this material. It contained 96.4% alpha cellulose, and the entire quantity was dried in a vacuum drying oven to about 3% moisture content, prior to use.

carbonate. The soda cellulose was transferred from the filter to a 50-cc. round-bottomed flask fitted with a ground-glass condenser connection, 16 gm. of *o*-chlorobenzyl chloride added, and the mixture heated in an oil thermostat at the required temperature for a definite time interval. The purification of the reaction products was varied somewhat before a final procedure was arrived at, and will be described for each experimental series. Before analysis, the products were dried for 12 hr. at 80° C. and 20 mm. pressure in a slow stream of air drawn through a phosphorus pentoxide drying train. This drying procedure was found to be thoroughly efficient.

(c) *Reaction Time Series*

The procedure used in this series of experiments was standard, with conditions set as follows:— sodium hydroxide concentration, 20 gm. per 100 cc.; steeping time, two hours; reaction temperature, 90° C.; reaction time, variable. The products were purified in such a way as to recover both the soluble and insoluble ethers in one fraction. To effect this, a large excess of 95% alcohol was added to the reaction mixture to precipitate any cellulose ether which was dissolved in it. The products were then recovered by filtration, and washed thoroughly with alcohol, with water, again with alcohol, and finally with ether. The results of this series of experiments are summarized in Table I. The micro-Carius method was used in the analyses.

TABLE I  
RELATION OF REACTION TIME TO TOTAL ETHERIFICATION

Time, hr.	2	5	7.5	10	24
Cl, %	1.40, 1.09	4.43, 4.47	7.08, 6.80	7.90, 9.57	12.57
Mean	1.25	4.45	6.94	8.73	12.57

(d) *Reaction Temperature Series*

Two series of experiments were carried out in the investigation of this variable, a preliminary and final series. They were similar except in reaction time and purification of the products. The preliminary series was run immediately after the four preliminary experiments, before the discovery of the solubility of the higher *o*-chlorobenzyl ethers of cellulose in the reaction mixture.

*Preliminary series.* The reaction procedure used was standard, with the conditions set as follows:— Sodium hydroxide concentration, 19.9 gm. per 100 cc.; steeping time, two hours; reaction temperature, variable; reaction time, seven hours. The purification procedure permitted of recovery of the insoluble ethers, contaminated by as much of the soluble ethers as was not removed by solubility in the reaction mixture. The reaction mixture, on cooling, was filtered, and the residue on the filter thoroughly washed with alcohol, water, alcohol, and ether, dried, and analyzed by the micro-Carius method. The results are presented in Table II.

TABLE II  
 EFFECT OF REACTION TEMPERATURE ON ETHERIFICATION (PRELIMINARY)

Temp., °C.	75	81	88	95	108	120	130
Cl, %	1.09 1.29	2.15 2.12	4.90 4.68	6.38 6.84	6.97 6.89	7.19 7.59	10.88 11.04
Mean	1.19	2.13	4.79	6.74	6.93	7.39	10.96

That the above figures, with the exception of the values at 130° C., represent substantially the chlorine content of the insoluble cellulose ethers, can be shown from the data to be presented on the final temperature series in Table III. Reference to this table shows that up to 120° C. only 160 mg. of soluble ethers could be present in a total ether yield of about one gram. Part of these soluble ethers would be lost by their solubility in the reaction mixture. Therefore it may be concluded that, in the figures presented in Table II, and plotted in Fig. 2, curve No. 1, contamination of these insoluble products by soluble cellulose *o*-chlorobenzyl ethers could cause only a very slight increase in their chlorine content. This is not the case in the experiment carried out at 130° C., since a much greater amount of soluble ether is formed at this temperature, and the reaction mixture is more difficult to filter. However, it may be said that, with the exception of the value at 130° C., the figures presented in Table II and plotted in Fig. 2, curve No. 1, represent substantially the effect of reaction temperature on the formation of insoluble cellulose *o*-chlorobenzyl ethers during a seven-hour reaction.

*Final temperature series.* The reaction procedure used in this series of experiments was standard, with the conditions set as follows: — Sodium hydroxide concentration, 19.9 gm. per 100 cc.; steeping time, two hours; reaction temperature, variable; reaction time, 10 hr. The purification procedure permitted of a separation of the products into soluble and insoluble fractions in the following manner. The reaction mixture was filtered and the washing of the insoluble material carried out as described in the preliminary temperature series. The soluble ether remaining in this fibrous part was then removed by a three-hour continuous extraction with chloroform. The insoluble residue from this extraction was thoroughly washed with alcohol and ether, and given the usual drying, and constituted the *insoluble* cellulose *o*-chlorobenzyl ether fraction. To recover the dissolved cellulose ether, the filtrate from the reaction mixture was added to 150 cc. of petroleum ether (b.p., 30–50° C.) and allowed to stand for several hours, during which period the precipitated product coagulated and settled to the bottom of the flask. This precipitate was filtered off, washed with alcohol, and dissolved in the chloroform which was used in the extraction of the insoluble product. This chloroform solution, which now contained all the *soluble* cellulose *o*-chlorobenzyl ether, was dropped slowly into a flask containing rapidly stirred, boiling water. This removed the chloroform and precipitated the cellulose ether in granular form. The product from this precipitation was ground to a fine powder in an

agate mortar, thoroughly washed with alcohol, and given the usual drying. The results of the experiments in this final temperature series are shown in Table III.

TABLE III  
EFFECT OF REACTION TEMPERATURE ON ETHERIFICATION (FINAL SERIES)

Temperature °C.	Insoluble ethers		Soluble ethers	
	Yield, gm.	% Cl*	Yield, mg.	% Cl**
20	0.86	0	0	
60.5	0.84	0.4	0	
75.5	0.80	2.41	0	
82.5	0.88	5.60	0	
89	0.99	9.19	30	15.27
92	1.07	10.47	45	15.41
95	1.12	11.18	65	15.52
105	1.21	11.67	50	15.41
112	1.30	12.00	60	15.55
120	1.10	12.35	161	15.82
135	1.03	11.27	260	16.42

Method of analysis:— \*Robertson; \*\*Willard and Thompson.

(e) *Alkali Concentration Series*

The reaction procedure used in this series of experiments was standard, with the conditions set as follows:— Sodium hydroxide concentration, variable; steeping time, two hours; reaction temperature, 95° C.; reaction time, 10 hr. The purification procedure was the same as that used in the final temperature series, this permitting of a separation of the products into soluble and insoluble ethers. The analysis of the products is given in Table IV.

TABLE IV  
EFFECT OF ALKALI CONCENTRATION ON ETHERIFICATION

Concentration, gm. NaOH/100 cc.	Insoluble ethers		Soluble ethers	
	Yield, gm.	% Cl*	Yield, mg.	% Cl**
8.6	0.98	4.62	0	
13.6	1.12	9.31	13	15.27
15.6	1.14	10.05	32	15.38
20.6	1.09	11.09	60	15.55
23.9	1.12	11.38	72	15.66
25.2	1.09	11.30	78	16.12
29	1.01	10.89	145	16.14
36.9	0.84	8.71	170	16.72
43.1	0.72	6.07	190	15.26
50.8	0.66	3.87	150	17.26

Method of analysis:— \*Robertson; \*\*micro-Carius.

(f) *Series on Time of Steeping*

The reaction procedure used in this series of experiments was standard, with the conditions set as follows:— sodium hydroxide concentration, 18.9 gm. per 100 cc.; steeping time, variable; reaction temperature, 95° C.; reaction

time, 10 hr. The purification procedure was the same as that used in the final temperature series, permitting of a separation of the products into soluble and insoluble ethers. The analysis of the products is presented in Table V.

TABLE V  
EFFECT OF TIME OF STEEPING ON ETHERIFICATION

Steeping time, hr.	Insoluble ethers		Soluble ethers	
	Yield, gm.	% Cl*	Yield, mg.	% Cl**
1/12	1.15	11.24	60	15.70
1/2	1.14	11.01	60	15.73
2	1.12	11.18	65	15.52
12	1.14	11.09	55	14.14
48	1.12	10.83	50	14.14

Method of analysis:— \*Robertson; \*\*Willard and Thompson.

(g) *Effect of Increasing Alkali Concentration and Reaction Temperature Simultaneously*

Two experiments were run to check this point.

(1) The reaction procedure used was standard, with the conditions set as follows:— sodium hydroxide concentration, 50 gm. per 100 cc.; steeping time, two hours; reaction temperature, 120° C.; reaction time, 10 hr. The purification procedure permitted of the separation of the products into soluble and insoluble ethers, but had to be modified from that previously used for this purpose because the fibrous structure of the product was destroyed to such an extent that it was impossible to filter the reaction product. The products were therefore purified in the following way. The reaction mixture was subjected to steam distillation for four hours to remove as much of the *o*-chlorobenzyl chloride as possible. The pasty product from this procedure was then given a four-hour extraction with chloroform in a Soxhlet apparatus. The insoluble residue, after the usual washing and drying, weighed 0.26 gm., and contained 4.53% chlorine.

The usual method of precipitating the soluble ethers from the chloroform solution gave a plastic product which could not be powdered or purified by washing. This was probably due to small amounts of *o*-chlorobenzyl chloride and *o*-chlorobenzyl alcohol which had not been removed by the steam distillation. The plastic product was therefore incorporated in a mortar with a large amount of crystalline sodium chloride, and given a four-hour extraction with alcohol in a Soxhlet apparatus. The salt was then removed from the extracted material by washing with water, and the soluble cellulose ether recovered as a powder with none of its previous plastic properties. The soluble *o*-chlorobenzyl ether of cellulose recovered from this reaction weighed 1.02 gm., and on analysis showed:— Cl; 16.97, 16.74%; mean, 16.85%.

(2) In the second of these experiments the reaction procedure used was standard, except that the quantities in each case were five times larger. The

reaction conditions were:—sodium hydroxide concentration, 70 gm. per 100 cc.; steeping time, 15 min.; reaction temperature, 120° C.; reaction time, 15 hr. The purification of the products was carried out in the same way as in the previous experiment except that the removal of impurities by incorporation with salt and alcohol extraction was carried out immediately after the steam distillation, and was then followed by the chloroform extraction. A yield of 0.65 gm. of insoluble product was obtained, showing the following analysis by the method of Robertson:—Cl, 9.17, 9.08%; mean, 9.12%. A yield of 6.6 gm. of soluble ether was obtained, giving the following analysis by the method of Willard and Thompson:—Cl: 16.60, 16.61%; mean, 16.60%.

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## SOME CONSIDERATIONS IN REGARD TO EXPERIMENTS WITH CHEMICAL HERBICIDES<sup>1</sup>

BY GEO. L. GODEL<sup>2</sup>

### Abstract

The writer reviews the subject of weed control by chemicals in the growing crop mainly with reference to prairie conditions, and discusses it under the following heads: the herbicide, the sprayer, weather conditions, the crop, the experimental technique. A technique is described which permits the analysis of a large group of variable factors in the weed-control experiments carried on in Saskatchewan.

An extensive program of weed research was undertaken in Saskatchewan in 1929, to determine the practicability of both methods of control by chemicals (control of perennial weeds in small patches, and control of annual weeds in the crop) under semi-arid conditions and with extensive farming methods. The experiments were conducted under the most variable conditions of soil and climate, and many chemical solutions were tested at varying concentrations and amounts of spray per acre. Treatments were made on stinkweed and wild mustard in wheat, oats, barley, rye, corn, sweet clover, western rye grass, alfalfa and brome grass. During the last three years the effects of the following chemicals have been studied: sodium chlorate, sodium dichromate, copper nitrate, copper sulphate, sulphuric acid, iron sulphate, sodium chloride and ammonium bisulphate. All of these, except the last, reduced the weed infestation of the treated crops; the chemicals are listed in order of effectiveness. The results showed, however, that many factors other than proper strength of solution and amount of spray per acre should be taken into account.

The largest percentage of control of wild mustard in the crop of 1931 was obtained with weak solutions of sodium chlorate. The effects of this chemical on the crop are more severe than those of the others, and therefore its use should be further investigated before it can be recommended.

The application of dry chemicals for control of weeds in the crop combine in general two farming operations—fertilizing of the soil and weed control. These methods offer little promise for Saskatchewan as they require cool, foggy, wet weather which is rarely found in the west, and because it has been found that, in order to be effective here, commercial fertilizers have to be drilled in with the seed and not broadcasted on the surface.

It appears that, under Saskatchewan conditions, only a few weed species can be controlled successfully. In wheat, sulphuric acid will control common wild mustard, Indian mustard, wild radish, stinkweed, false flax, tumbling mustard and wild buckwheat. New shoots of Canada thistle are somewhat retarded in their development. Hare's ear mustard, ball mustard, cow cockle, lamb's-quarters, Russian pigweed, and the grasses, wild oats, darnel, etc., could not be controlled under the conditions of these experiments. It is thus important that chemical treatments be limited to fields where weed infestation consists mostly of susceptible weeds, because in controlling these the crop and resistant weeds are stimulated. At Watson, Sask., in 1931, when wild mustard or stinkweed was associated with either wild oats, lamb's-quarters or Russian pigweed, there was always an increase in the development of the latter weeds after treatment.

In these experiments the cereals ranked as follows in resistance to sulphuric acid sprays:—resistant; wheat, oats: intermediate; barley, spring rye: susceptible; corn.

### Introduction

Weed control experimentation with herbicides is carried along two different lines; the control of perennial weeds in small patches, and the control of annual weeds in the crop. These two methods are absolutely distinct in that one aims at complete eradication of the root system of troublesome perennial weeds, it renders the soil barren for an indefinite period of time and it is expensive and therefore limited to the treatment of weeds in small patches in

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<sup>2</sup> Weed Research Investigator, Field Crops Branch, Saskatchewan Department of Agriculture.

the field, or on land inaccessible to cultivation. The other method is intended for the control of certain annual weeds in a crop; it causes little injury to the latter and no harmful effect to the soil; it is cheap and intended for the treatment of large areas thoroughly weed-infested.

Annual weeds are troublesome in a field because they compete with the crop for mineral nutrients, space, light, and especially soil moisture, a limiting factor in crop production in western Canada, and thus occasion a great loss in yield of harvested farm products. Most annual weeds are probably still more troublesome because of their earliness which allows them to shatter their seeds in the field before harvest. Goss (30) has demonstrated that most weed seeds possess the ability to retain their viability over long periods of time, and a tendency to delayed germination.

Weed control by chemicals may become of considerable importance to prairie farmers for the control of wild mustard and stinkweed in a cereal crop because these weeds are extremely difficult to control by cultural methods.

The treatment of weeds in the crop fulfils two purposes: it favors the growth of the cereal because it almost eliminates weed competition; it also prevents weed seeds shattering before harvest and thus acts as a complement to good tillage, rendering possible in the course of time complete eradication of wild mustard and stinkweed on the farm.

Chemical control in the crop is a common practice on the larger farms of Europe where the method was first used; in America the method has been tried from time to time, but in spite of the recommendations of Bolley and others, it has never passed the experimental stage. In Saskatchewan, the Department of Agriculture undertook in 1929, in co-operation with the University of Saskatchewan, an extensive program of weed research to determine the practicability of both methods of control by chemicals under semi-arid conditions and with extensive farming methods. This work was later carried on in collaboration with the National Research Council of Canada and the Departments of Agriculture of the provinces of Alberta and Manitoba.

These experiments were conducted under the most variable conditions of soil and climate and many chemical solutions were tested at different concentrations and amounts of spray per acre. Treatments were made on stinkweed and wild mustard in wheat, oats, barley, rye, corn, sweet clover, western rye grass, alfalfa and brome grass.

The experiments have confirmed the author's deductions arrived at after an extensive survey of the literature. Both clearly indicated that weed control by chemical sprays in a growing crop is subject to the action of a large number of factors, the importance of which must be realized if successful control is to be obtained in all cases.

The writer has attempted to review the subject of weed control by chemicals in the growing crop, but mainly from the standpoint of prairie conditions. More experiments will be conducted in the next year or two but future trials will consist mostly of extensive field experiments to determine more accurately the cost of treatment per acre, and to study the relative value of the different types of spraying equipment.

The subject is discussed under the following heads: the herbicide, the sprayer, the weather conditions, the crop, the experimental technique.

### The Herbicide

A search of the literature indicates that a large number of chemicals can be used for the control of annual weeds in a growing crop. The methods of application of the chemicals can be grouped into two classes: chemical sprays and chemical dusts, broadcasted like most commercial fertilizers.

The most common methods in use belong to the first group. These in turn can be divided into: (a) acid sprays, which act by burning the plant tissues; (b) chemical sprays which are toxic to plants.

The application of dry chemicals for the control of weeds in the crop is of fairly recent date, but the results which are reported from Europe are most interesting and might prove of some value in the more humid districts of the American continent. These methods combine in general two farming operations; fertilizing of the soil and weed control. They offer little promise for Saskatchewan because, first, they require weather conditions which are rarely found in the west (cool, foggy, rainy weather); and second, because it has been proved that in order to be effective here, commercial fertilizers have to be drilled in with the seed and not broadcasted on the surface.

These different methods cannot be fully discussed in the scope of one article. The reader is referred to reports by the following investigators for further information:

*Chemical sprays*:—sulphuric acid; Rabaté (71), Aslander (4, 5): copper sulphate; Long (47), Bolley (10): copper nitrate; Dusserre (25, 26): iron sulphate; Korsmo (45), Olive (62), Shutt (84): sodium chloride; Marre (53, 54): sodium chlorate; Loyer (50).

*Dry chemicals*:—powdered sodium chloride; Crépin (20): kainit; Vasters (89): potassium bisulphate; Fron (29): ammonium sulphate, sylvanite and cyanamide; Jaguenaud (38-41).

Other chemicals which have been tested include chiefly ammonium chlorate, sodium nitrate, sodium arsenite, sodium dichromate, ammonium bisulphate, and sodium hydroxide.

In Saskatchewan, the following chemicals have been studied during the past three years: sulphuric acid, copper sulphate, copper nitrate, iron sulphate, sodium chloride, sodium chlorate, sodium dichromate, and ammonium bisulphate. All these chemicals, with the exception of ammonium bisulphate, considerably reduced the weed infestation of the treated crops, but the results indicated clearly that many factors other than proper strength of the solution and right amount of spray per acre had to be taken into consideration. In order of effectiveness pound per pound, disregarding such factors as cost of application, solubility of the chemical, etc., the above-mentioned chemicals seemed to rank as follows, under Saskatchewan conditions: sodium chlorate, sodium dichromate, copper nitrate, copper sulphate, sulphuric acid, iron sulphate and sodium chloride. To give similar results, these chemicals would therefore have to be applied at different rates and for the control of common

wild mustard, the factor which will determine their usefulness from a practical standpoint, will be price per pound of pure chemical. It takes for instance about six times as much sodium chloride as copper sulphate, five times as much iron sulphate as copper nitrate, five times as much sulphuric acid as sodium chlorate (amounts by weight). The amounts of spray and strength of the solution shown in Table I would give, under average conditions in Saskatchewan, similar control of wild mustard in wheat.

TABLE I  
CONCENTRATION AND QUANTITY OF SPRAY REQUIRED TO GIVE SIMILAR CONTROL OF WILD MUSTARD IN WHEAT UNDER AVERAGE CONDITIONS IN SASKATCHEWAN

Chemical	Concentration, %	Dosage per acre, gal.	Chemical	Concentration, %	Dosage per acre, gal.
Sodium chlorate	1½	75	Sulphuric acid	8	75
Sodium dichromate	3-3½	75	Iron sulphate	25	75
Copper nitrate	3½	75	Sodium chloride	25	125
Copper sulphate	5-5½	75			

The largest percentage of wild mustard control in the crop in 1931 was obtained with the application of weak solutions of sodium chlorate and such a treatment would have the great advantage of being the cheapest as far as cost of application is concerned, but the effect of this chemical solution on the crop is more severe than that of the other chemicals and the method has to be further investigated before it can be recommended.\*

Sulphuric acid treatment seems to injure the sprayed crop to a considerable extent, because it burns and bleaches most of the leaves which the cereal had formed at time of treatment: if the treatment is done early, the damage disappears long before harvest. Because of its mode of action on the weeds, sulphuric acid permits the control in the crop of more weed species than is the case with the other chemicals mentioned.

The use of copper nitrate is much restricted because of the high cost of the chemical.

Sodium dichromate should be used with caution because it acts somewhat by burning the plant tissues and also by its great toxicity.

Copper sulphate sprays are fairly advantageous but their use is limited exclusively to wild mustard and closely related species.

An experiment was carried out under controlled conditions in the greenhouse to determine whether repeated applications of copper salt sprays would be injurious to the productivity of the soil. It was calculated that 25 lb. of copper nitrate or copper sulphate was the amount of chemical required to

\*Treatments made in 1932 with weak solutions of sodium chlorate were not satisfactory. The crop was seriously injured, resulting in a considerable loss of yield of grain at harvest.

Another chemical, ammonium thiocyanate, under trial for the first time this season, ruined the crop completely.

In all other respects, the 1932 experiments confirm the writer's observations recorded in this paper.

spray one acre of weed-infested land. In consequence, provided there was no leaching of the chemical, no oxidation and no assimilation by the plants, there would be after ten treatments 250 lb. of pure copper salt per acre, after 40 treatments 1000 lb., etc.

The results, contrary to expectation, indicated that even the presence of 2500 lb. of copper sulphate, or copper nitrate per acre, was not injurious to plant growth. On the contrary, as indicated in Tables II and III, the chemical treatment stimulated plant growth, resulting in greater length of straw and longer heads. Somewhat similar results were obtained by Dr. J. D. Newton, at the University of Alberta.

TABLE II  
EFFECT OF COPPER SULPHATE ON THE HEIGHT AND LENGTH OF HEADS OF WHEAT PLANTS

Copper sulphate per acre, lb.	0	25-175	250-500	750-1000	1250-1500	1750-2000	2250-2500
Av. height of cereal, in.	20.7	21.7	21.9	22.2	22.0	22.6	23.7
Av. length of heads, cm.	4.50	5.20	5.29	5.50	5.82	6.12	6.17

Copper nitrate caused still greater stimulation owing probably to the action of the nitrate.

Iron sulphate and sodium chloride are less effective for weed control in western Canada than in districts with more humid climate and higher concentrations are required. This, added to a much higher cost of the chemicals because of transportation charges, makes their use in Saskatchewan prohibitive.

It can be seen that it is very difficult and indeed nearly impossible to state offhand the amount of spray and the degree of chemical concentration which will give best results in all cases. This depends much on the water supply, the degree of weed infestation, the state of development of both the weed and the crop at treatment, etc. The total amount of pure chemical applied per acre, however, is more stable and if, for instance, in the case of sulphuric acid an 8% solution by weight is suggested in amounts of 75 gal. per acre, it is possible to vary either way according to local conditions, using 100 gal. of a 6% solution or 50 gal. of a 12% solution. These concentrations are by weight.

### The Sprayer

The results depend to quite an extent on the spraying equipment. Cheapness and efficient application of the spray are factors to be considered when purchasing a sprayer for field use. Efficient application of the spray requires a high pressure (at least 100 lb.), an even pressure and an even application. Cost of application depends on capacity and construction of sprayer as well as economy of labor. High and even pressure are essential. Bolley (10) in 1908 wrote, "Ordinarily, the pump should deliver a pressure of 100 pounds or more per square inch, and there should be a gauge to show the pump pressure. I have not seen a machine which did good work with a lower pressure." This can easily be understood since, unless the spray is very fine, much of the solution will drop to the ground. If the water used in making the solution is not



strained properly, some of the nozzles become obstructed resulting in strips of untreated weeds. The height of the boom or spraying bars above soil level must be regulated according to the height of the weeds; if it is too low, the tips of the taller weeds will escape treatment.

Sulphuric acid sprays can be used only in specially constructed sprayers where all parts coming in contact with the liquid are brass, lead, wood or rubber.

### Weather Conditions

The lethal effect of a chemical spray depends to a great extent on the weather conditions. Aslander (5), spraying mustards with sulphuric acid solutions, showed that:

1. The weeds were killed under all moisture conditions but the results were best in dry air.
2. Increase in temperature gave increased efficiency.
3. Artificial rain applied one hour after treatment even with a weak solution did not decrease the action of the spray.

Dealing with iron sulphate, Aslander, in the same article, showed that contrary to sulphuric acid it was most destructive in an atmosphere of 100% relative humidity. Under such conditions a 5% solution applied on mustards in the greenhouse completely killed the plants in 24 hr. On the contrary, with a relative humidity of from 30 to 60% the solution sprayed upon the plants rapidly evaporated and crystals were formed on the surface of the leaf without injury to the plants. Solutions up to 15% gave similar results. Low atmospheric humidity is usual under western prairie conditions during the daytime, and Aslander's results well illustrate why it is found necessary in Saskatchewan to use a 25% solution of iron sulphate in place of a 10 or 15% solution as recommended by many European investigators.

Evaporation also plays some part as shown by the recent studies of Bissey and his coworkers (6). At a given temperature iron sulphate is more effective when dried slowly than quickly, while the contrary is the case with copper sulphate.

Weather conditions influence the results from chemical treatments in many other ways: they affect the degree of weed infestation of a field before treatment, the relative development of both weeds and crop, and their appearance. A heavy rainfall after treatment may cause the germination of a new lot of weed seeds or hasten the recovery of plants seriously injured but not killed.

In southern Saskatchewan in 1930, the amount of moisture stored in the soil was very small and this condition was aggravated by the excessive evaporation resulting from the high winds which prevailed in May and June. Crops and weeds which in general had started normally made little headway except in the depressions where moisture was more abundant. In the higher places, most of the weeds were not able to compete with the cereal; they dried out and disappeared before harvest. In 1931, near Watson, the opposite condition prevailed, moisture was scarce in early spring and the crops remained fairly free of annual weeds until the middle of June, when heavy showers fell in the district.



Soil moisture and temperature play a large part in determining the degree of weed infestation of a crop. In general if soil moisture is plentiful, but soil temperature unsatisfactory for the germination of the cereal (a condition which often prevails when seeding is done too early), the weeds get ahead of the cereal and the reduction in yield at harvest is considerable. If on the other hand both moisture and temperature are favorable for germination of the cereal, most of the weeds will be smothered.

In years of low precipitation and limited soil moisture one of two conditions will be found: the top layer of the ground is dry and at a depth of 2 or 3 in. there is just enough moisture to permit the germination of the cereal and the crop at harvest will be clean. If the soil down to, for instance, 4 in. is too dry for germination of either weeds or crop, the first rain unless unusually heavy will germinate only the weeds near the surface and this crop at harvest will be very weedy and the loss excessive.

### The Weed

The method of weed control by chemicals in the crop is based on the relative resistance of plants to chemical sprays. It is thus essential to know what is the susceptibility of both weeds and crops at different stages of development under conditions of soil and climate prevailing in a district.

Aslander (5) showed that under ordinary conditions a sulphuric acid solution penetrates the tissue rapidly, kills the cytoplasm without causing plasmolysis, decomposes the chlorophyll as it unites with the magnesium atom in the chlorophyll molecule, and destroys the chloroplasts. The cell walls are generally not affected except on very young leaves. More acid is needed to kill leaves with thick cell walls (such as in the case of winter annuals) than the thin leaves of young plants. Weeds grown in the greenhouse are more readily killed than weeds grown in the field. Weeds with waxy leaves such as hare's-ear mustard, are more resistant than plants such as common wild mustard and stinkweed. Plants of the grass family whether cereals or weeds are all fairly resistant to weak chemical solutions because their leaves are in most species narrow and waxy and because also, at time of spraying, the growing point is still well protected.

In the case of chemicals which are toxic, action is much less rapid than in the case of sulphuric acid. The essential factor in the susceptibility of the weeds to toxic sprays is ability of the weed to retain the spray for a certain length of time; if the leaves are small or very smooth, the droplets of spray will run off rapidly and the treatment will not be satisfactory. This explains why stinkweed, which is just as susceptible to sulphuric acid sprays as wild mustard, cannot be controlled successfully in a crop with copper sulphate or iron sulphate, while common wild mustard can.

The number of weed species which can be controlled in a crop depends directly on the resistance of the crop, which is greater in Europe where winter cereals are grown. The latter are more resistant to chemical sprays than spring cereals. Under Saskatchewan conditions, it appears that only a few species can be controlled successfully. In wheat, sulphuric acid will control

common wild mustard, Indian mustard, wild radish, stinkweed, false flax, tumbling mustard, and wild buckwheat. New shoots of Canada thistle are somewhat retarded in their development; hare's-ear mustard, ball mustard, cow cockle, lamb's-quarters, Russian pigweed and the grasses, wild oats, darnel, etc., were not controlled under the conditions of the author's experiments. It is thus important that chemical treatments be limited to such fields where weed infestation consists for the largest part of susceptible weeds, for the simple reason that in controlling the susceptible weeds, we stimulate not only the crop, but also the resistant weeds. At Watson, Saskatchewan, in 1931 when wild mustard or stinkweed was associated with either wild oats, lamb's-quarters, or Russian pigweed, there was always an increase in the development of the latter weeds after treatment.

For plot experiments it is best to select fields with only one weed species dominant, for instance, either common wild mustard or stinkweed. Uniformity in the kind of weed infestation however is not enough, and uniformity in the degree of weed infestation of the plots is necessary when it is desired to submit the yield data to biometrical tests of significance.

Let us first consider the effect of variable weed infestation on the yield of harvested grain and then see how variable yields affect the biometrical analysis.

An experiment conducted by the writer both in 1930 and 1931 under field conditions, to determine the effect of variable degrees of wild mustard infestation on the yield of wheat at harvest showed conclusively:

1. That even a light weed infestation causes a reduction in the yield of harvested grain.

2. That an increase in the number of mustard plants per unit area causes a steady decline in the yield of the grain, in spite of the fact that the mustard plants are smaller and set less seed. The results of this experiment for 1931 are summarized in Table III.

TABLE III  
EFFECT OF VARIABLE DEGREE OF WILD MUSTARD INFESTATION ON THE YIELD OF WHEAT AND WILD MUSTARD AT HARVEST. WATSON, SASKATCHEWAN, 1931

Group No.*	Average no. of mustard plants per sq. ft. area	Wheat, gm. per sample	Mustard		
			Pure seed, gm. per sample	Av. weight per plant	Av. weight seed per plant
1	0-1	1110	43.6	3.18	.65
2	2-3	974	186.4	2.39	.58
3	4-5	942	285.3	2.01	.49
4	7-9	886	342.	1.42	.33
5	12-15	780	461.1	1.16	.26

\*Eight plots per group.

The following example will indicate how a variable degree of weed infestation makes it difficult to study the yield data biometrically.

Let us assume two series of plots, treated and untreated, in which all factors are uniform except the number of weeds per unit acre, and that the counts per

square foot at time of treatment were as follows:

Check plots	5	15	21	9	12	1
Treated plots	7	5	14	11	19	4

Let us then assume that in this case the chemical treatment was 100% effective so that after treatment no weeds remained alive in the treated plots. The respective counts after treatment would then be as follows:

Check plots	5	15	21	9	12	1
Treated plots	0	0	0	0	0	0

It is quite conceivable and indeed probable that the difference between average yields taken from the two series of plots would not be statistically significant. The first and last of the treated plots might easily show a decrease in yield, while the individual differences between the other pairs would be so variable that a biometrical analysis would fail to establish confidence in the results owing to the existence of an uncontrollable factor; in this case, the degree of weed infestation.

This can be illustrated by some results obtained at Drinkwater, Saskatchewan, in 1930. A treatment with sulphuric acid of common wild mustard in wheat was made in duplicated plots, one acre in area, and three samples, each of 50 sq. ft., were taken in each plot. By the pairing method, the calculation was as shown in Table IV.

TABLE IV

Samples from		Difference	(Difference) <sup>2</sup>	Samples from		Difference	(Difference) <sup>2</sup>
Treated plots, gm.	Untreated plots, gm.			Treated plots, gm.	Untreated plots, gm.		
767	798	- 31	961	735	574	+161	25921
1040	1015	+ 25	625	866	936	- 70	4900
1028	736	+292	85264	1197	885	+312	97344

$$\text{S.D. difference} = \sqrt{\frac{215015}{6} - \left(\frac{689}{6}\right)^2} = 150.48$$

$$\text{S.D. mean diff.} = \frac{150.48}{\sqrt{5}} = 67.39$$

$$t = \frac{114.63}{67.39} = 1.8$$

For  $n=5$ , the  $t$  value of 1.8 does not indicate that the difference in yield of grain between treated and untreated plots is significant, although four out of six samples show an increase in yield and the average increase for all samples is 3.68 bushels per acre, or 12.6%. This indicates that unless the weed infestation is very uniform, it is very difficult to show biometrically significant results, and the only remedy is to take a greater number of samples at harvest.

It is difficult to say offhand when the chemical treatment of weed-infested fields should be recommended because this depends on many things; mainly the kind of weed, the degree of infestation, the growth of the weed in relation

to the crop, the kind of crop, the value of the crop, etc. In the case of wild mustard or stinkweed in wheat, a treatment with sulphuric acid will always be a remunerative operation if the infestation is severe.

With moderate infestation, it will be advantageous to make the treatment only if the weed has got an early start and if there is a danger of it overcrowding the cereal. In the case of light weed infestation, treatment should not be made unless the farmer can afford the extra expense of weed control, because it is not likely that the treatment will result in an increased yield.

In years when the price of grain is low, it will be economical to treat only the more heavily infested fields. On the contrary when grain commands a high price on the market, treatments will be advantageous also on less heavily infested fields because a small increase in yield of grain is all that will be required to balance the cost of the treatment.

### The Crop

Chemical treatments of weeds in the crop are generally confined to the cereals. In the author's experiments, the cereals ranked as follows for resistance to sulphuric acid sprays:

Resistant	Intermediate	Susceptible
Wheat Oats	Barley Spring rye	Corn

Winter wheat is however more resistant than spring wheat and all cereals are most resistant to chemical sprays at their early seedling stage (three-leaf stage). The fact that barley is less resistant than either wheat or oats was clearly indicated in both the 1930 and 1931 experiments. In 1931 for instance a treatment was made under the most favorable conditions, but there was a significant decrease in yield of the treated portion of the field over the untreated portion. In any case, it is probable that it would not be profitable to spray a field of barley because that crop is able to compete more satisfactorily with the weeds than any of our other cereals.

Other crops than those already mentioned can be sprayed. All grasses for instance are fairly resistant and this permits the control of some weeds in pastures, meadows, lawns, etc. Spraying has been resorted to by gardeners to replace weeding of such truck crops as onions, leeks, etc. Long (47) states that 40 gal. of a 4% solution of copper sulphate per acre does not permanently injure peas, beans, clover, etc. Urban (86) found that red clover (*Trifolium pratense*) is quite resistant to a 5% solution of sulphuric acid (by volume), at the rate of 100 gal. of spray per acre, when the plants have formed their fourth leaf. The spray will, of course, burn these leaves and the upper part of the stem, but the legume quickly recovers. As far as alfalfa is concerned, treatment is also safe after the crop has reached the fourth-leaf stage, but this is somewhat later than in the case of red clover.

At Drinkwater, Saskatchewan, in 1930, successful control of wild mustard

with a 4½% solution of sulphuric acid was obtained in crops of western rye grass, alfalfa and sweet clover sown without a nurse crop, but considerably more experiments are required before treatment of sweet clover, alfalfa or flax can be safely recommended under Saskatchewan conditions.

The cereal should be sprayed before it is in the shotblade and whenever possible in its third- to fourth-leaf stage, when the seedlings recover most rapidly and the weeds are well exposed to the direct action of the spray. In general it can be said that the injury caused by chemical sprays to the cereal is in direct relation to its development, and this is indicated in Table V, which gives the summarized results of treatments of wild mustard in wheat at different stages of plant development, and in Tables VII to XII.

TABLE V  
AVERAGE YIELD OF WHEAT FROM TREATED AND UNTREATED PLOTS

Period	Check	Treated with H <sub>2</sub> SO <sub>4</sub>	Diff. in % of check	Check	Treated with CuSO <sub>4</sub>	Diff. in % of check
June 5-20	224.2	208.7	-7	161.1	218.5	34.5
June 21-July 2	196.1	166.2	-15.2	162.0	172.5	+ 6.5
July 3-21	170.9	120.0	-29.8	172.5	159.5	- 7.5

These treatments are not quite comparable, because the acid solution was actually stronger than the copper sulphate solutions. The data, however, clearly indicate that the amount of injury increases directly with the development of the crop.

In general, treatments made early in fields of wheat or oats heavily infested with wild mustard, stinkweed or some other weed susceptible to chemical sprays, result in increase in the yield of grain at harvest. On the other hand, late treatments cause a decrease in yield of grain for the double reason that the weed has then already caused much damage and the cereal does not recover as well from the injury sustained.

Evidence of the beneficial action of chemical treatments on yield of grain alone can be found in a great many articles on the subject. Reference is made, however, mainly to the work of Korsmo (45) whose summarized results are given in Table VI.

TABLE VI  
AVERAGE INCREASE IN YIELD OF WHEAT OBTAINED BY KORSMO IN THE COURSE OF EXPERIMENTAL WORK WITH HERBICIDES IN GROWING CROPS

Treatment with	Number of tests	Average increase in yield in % of untreated
Sulphuric acid, sprayed	676	26.5
Iron sulphate, sprayed	680	23.6
Nitric acid, sprayed	122	23.3
Calcium cyanamide, dusted	630	23.9



Following are tabulated some of the results obtained from spraying experiments at Watson, Saskatchewan, in 1931.

TABLE VII

EARLY TREATMENT OF STINKWEED IN WHEAT WITH SULPHURIC ACID;  
8% BY WEIGHT, 75 GAL. PER ACRE

	Grams per sample (average weight)		Difference in % of check
	Treated	Untreated	
Wheat	701	536	+30.8
Stinkweed seed	15	271.6	-94.5

TABLE VIII

MEDIUM LATE TREATMENT OF STINKWEED IN WHEAT WITH SULPHURIC ACID; 6% BY WEIGHT,  
100 GAL. PER ACRE, STINKWEED INFESTATION UNUSUALLY SEVERE

	Grams per sample (average weight)		Difference in % of check
	Treated	Untreated	
Wheat	396	168.5	+135
Stinkweed seed	34.3	305.8	- 88.8

TABLE IX

LATE TREATMENT OF STINKWEED IN WHEAT WITH SULPHURIC ACID;  
6% BY WEIGHT, 100 GAL. PER ACRE

	Grams per sample (average weight)		Difference in % of check
	Treated	Untreated	
Wheat	249.0	343.2	-27.4
Stinkweed seed	19.1	55.6	-65.7

TABLE X

EARLY TREATMENT OF COMMON WILD MUSTARD IN WHEAT WITH COPPER  
SULPHATE; 4% BY WEIGHT, 90 GAL. PER ACRE

	Grams per sample (average weight)		Difference in % of check
	Treated	Untreated	
Wheat	140.2	122.9	+14.1
Wild mustard seed	0.5	5.8	-91.4

TABLE XI  
MEDIUM LATE TREATMENT OF COMMON WILD MUSTARD IN OATS WITH  
COPPER SULPHATE; 5% BY WEIGHT, 100 GAL. PER ACRE

	Grams per sample (average weight)		Difference in % of check
	Treated	Untreated	
Oats	360.7	347.7	+ 3.7
Wild mustard seed	3.8	22.6	-83.3

TABLE XII  
LATE TREATMENT OF COMMON WILD MUSTARD IN WHEAT WITH COPPER  
SULPHATE; 3% BY WEIGHT, 100 GAL. PER ACRE

	Grams per sample (average weight)		Difference in % of check
	Treated	Untreated	
Wheat	185.4	184.2	+ 0.9
Wild mustard seed	30	47.8	-37.2

Another condition seems necessary to ensure the full benefit of a chemical treatment. This involves the rate of seeding of the crop in a weed-infested field. New weed seeds are always likely to germinate after treatment and unless the rate of seeding is sufficiently heavy, they will not be kept under control. This was evident in 1931 when comparing the amount of mustard seed harvested from treated fields where the rates of seeding were different.

In Europe benefits other than weed control and increased yield of grain are often obtained from chemical treatment. In 1923 Rabaté (69) reported that a field of winter wheat treated with a 10% solution of sulphuric acid (by volume), at the rate of 100 gal. of spray per acre, showed a relative freedom of yellow stripe rust over the untreated field. In 1927 Rabaté (73) wrote, "Our observations both from experimental work and from general field treatments, covering every year since 1912 thousands of hectares, indicate a very marked efficacy of sulphuric acid solutions at strengths of 10 to 14%, 65°Baumé, (by volume) against foot rot of wheat."

Urban (87, 88) made a study of this indirect action of chemical treatment which consists in lessening the injury from plant diseases. He observed that light, temperature and proper aeration are factors favoring the resistance of plants to diseases, and he has shown experimentally that the sulphuric acid treatment favored the factors causing plant resistance to diseases. High atmospheric humidity, for instance, is essential for quick rust development and there is no doubt that in years of abundant moisture a heavy weed infestation and a greater leafiness of the cereal creates within the crop ideal conditions for the development of the disease. On the contrary the removal of the weeds and of a proportion of the cereal leaves causes better ventilation, and improves the

light and temperature conditions within the crop. This lowers the humidity and creates a condition less favorable to the development of rust. Urban explains in the same way the greater resistance of cereal treated with sulphuric acid to *Erysiphe graminis*, *Leptosphaeria*, *Herpotrichoides* and *Ophiobolus graminis*.

### Experimental Technique

Very little information is available in the literature on experimental methods for weed control in the crop. The papers which have been published seem to indicate that with some exceptions few attempts have been made to conduct these experiments in a true scientific manner, with due consideration for the many factors which influence them. Besides, most investigators have worked independently. In general, it was necessary for the investigators to rely entirely on manufacturers for free use of equipment and chemical supplies, and on the farmer for free labor and data recordings. A special effort should be made to place weed-control experiments on a higher standard. Biometry must be used to test the significance of yield data but this necessarily involves a complete reconsideration of the experimental methods generally adopted. Whether this can be done in all cases remains to be seen, in view of the presence of such a large group of variable factors as we have attempted to describe in the preceding pages. The Subcommittee on Chemical Experiments of the Associate Committee on Weed Control of the National Research Council has, during the past three years, given some consideration to the question of suitable experimental procedure, and the following technique is to be used by the writer for the 1932 weed control program in Saskatchewan.

### Field Technique

#### Choice of Land

The experimental field must be as uniform as possible in soil and weed infestation. The latter is especially desirable and the weeds should be in the main of one species.

#### Plot Layout

Three points should be considered in deciding upon a suitable plot arrangement: (1) the object of each experiment; (2) the number of tests in each experiment; (3) the amount of uniform available land.

According to the object of the experiment we can recognize three types as follows:

A. Experiments which require much precision:—example, a study of the comparative value under definite climatic conditions of a few of the most promising herbicides. In this case the plots should be randomized and a large number of replicates used. The plots should be small, 10 by 20 ft., and arranged in a Latin square. When more than eight treatments are to be compared, the Latin square being no longer practical as it would involve too many replicates, we may use the Randomized Block arrangement with four to six replicates according to available space and help.

B. When the information sought is of a more general nature and involves a

great many different treatments:—example, an experiment to determine the relative effect of a chemical when applied at various concentrations and amounts per acre. A satisfactory method is that called the alternate check arrangement. This method has been used both in Alberta and in Saskatchewan in 1931 and consists in grouping the different experiments in a series of experimental blocks, where treated plots alternate with untreated plots. The chief advantages of this method are that it facilitates a direct comparison between treated and untreated plots and gives a fair index of the soil heterogeneity. Treatments should be at least in duplicate within each block.

C. For ordinary field trials, when only one chemical solution is used at a definite concentration, the best procedure may be to spray in strips leaving as many areas of untreated as there are of treated crop.

#### *Border Effect*

When the plots are separated by pathways it is generally found that many weeds develop after treatment at the edge of the plots. Care should thus be taken at harvest not to include in the samples portions of the crop within a distance of one foot from a road or pathway.

#### *Counts on Weeds*

The efficacy of a chemical solution is often based on the percentage of weed seedlings killed at treatment. The author's experience in Saskatchewan indicates that this method is not satisfactory. In some cases, the percentage of apparent kill at treatment was high with but little reduction in the amount of weed seeds in the crop at harvest. In other cases there were few seedlings killed per unit area but a great reduction in the amount of weed seeds in the crop at harvest. The fact is that complete destruction of the weeds depends on a great many factors, mainly:—the number of weeds per unit area, their development, the relative vigor and density of the crop. It is usually the case, when the weed infestation is severe, that the weeds are not killed outright because the spray does not reach all of the lower leaves. The ultimate result often is about the same as if they had been killed, because it takes nearly as long for the treated weeds to recover as for a new lot of seeds to germinate.

The usual method for counts of weeds is to select, in each plot, two or three square foot areas fairly representative of both weed and crop. These are staked out and the weeds therein counted again a few days after treatment. Better results would evidently be obtained if the counts could be made on larger areas, but when a large number of plots is involved this is out of the question. Difficulty arises in determining the time at which the second count should be made as it depends much on the chemical used; with sulphuric acid the effect on the weed is rapid but not lasting and the plants considered as killed often recover; in the case of iron sulphate the contrary may occur, and plants considered as alive two days after treatment often dry out later with further action of the chemical. Other inconveniences arise when new weeds germinate after treatment and are recorded in the second count.

#### *Sampling*

A better method to judge the efficacy of a chemical treatment in the crop

consists of sampling the plots at harvest for both weed-seed content and yield of grain. Two or three representative areas, approximately 25 sq. ft. each, are selected in each plot. First the weeds are pulled by hand, special care being taken to avoid shattering, and then the crop is cut with a sickle. Weeds and crop must be bagged, threshed and analyzed separately. In the case of stinkweed, which shatters quite early, hand pulling should be done from two to three weeks before harvest.

This method of estimating the actual decrease in weed infestation of a crop provides the investigator with much valuable information. It has, however, one disadvantage in that it somewhat underestimates the actual effectiveness of the herbicide. At harvest most of the weeds from untreated plots are matured and their seeds ready to shatter, while weeds left in the treated plots are usually very green. If harvest operations are not too long delayed, these seeds will not shatter to any appreciable extent in the field but will be retained by the plants until threshing.

#### *Recording of Data*

The following points are recorded on the standard record sheets designed by the Subcommittee on Chemical Experiments:

*Before treatment:* size of plot, kind of crop, date of seeding, rate of seeding, type of soil.

*At treatment:* stage of crop development, stage of weed development, average number of susceptible weeds per sq. ft., average number of other weeds per sq. ft., date of treatment, time of treatment, chemical applied, strength of solution, amount of spray per acre, weather conditions, soil moisture.

*After treatment:* percentage of susceptible weeds killed, weeds not affected, effect on the crop seedlings.

*At harvest:* height of crop, date crop matures, height of weeds, yield of grain, yield of weed seeds.

*After harvest:* weight of 1000 kernels of cereal, size of kernels, general appearance of kernels, occasional milling and baking tests.

In 1930, wheat from plots treated with sulphuric acid, copper sulphate, copper nitrate and sodium dichromate was tested by Dr. Larmour at the University of Saskatchewan, for its milling and baking quality. The results clearly indicated that while the treatment often reduced the size of the kernels, it had no effect on the milling and baking quality of the grain.

#### *Interpretation of Yield Data*

The biometrical method used to interpret yield data depends on the plot arrangement. The author has suggested four types of plot arrangement and accordingly four different biometrical methods for analyzing the data. The Latin square and the Randomized Blocks arrangement present no difficulty and may be treated by the method described by Goulden (31, 32).

With the alternate check system the significance of yield data may be established by taking differences between paired values directly, as suggested by Student, or from the probable error in percentage of the mean of all the

checks in an experiment. The first method seems preferable and is illustrated below:

Three samples, including all weeds and crop from 25 square foot areas, are taken in each plot. We have within each block every treatment in duplicate ( $t$  and  $T$ ) and, on the other hand, one untreated plot on either side of the treated plots ( $c$  *ca*  $C$  *Ca*). The significance of yield data is obtained by taking differences between paired values directly, there being altogether twelve pairs of samples for each duplicated treatment as follows:

$t_1$	$c_1$	$t_1$	$ca_1$	$T_1$	$C_1$	$T_1$	$Ca_1$
$t_2$	$c_2$	$t_2$	$ca_2$	$T_2$	$C_2$	$T_2$	$Ca_2$
$t_3$	$c_3$	$t_3$	$ca_3$	$T_3$	$C_3$	$T_3$	$Ca_3$

$c_3$	$t_3$	$ca_3$		
$c_2$	$t_2$	$ca_2$		
$c_1$	$t_1$	$ca_1$		

$c \quad t \quad ca \quad x \quad cb$

$C_3$	$T_3$	$Ca_3$		
$C_2$	$T_2$	$Ca_2$		
$C_1$	$T_1$	$Ca_1$		

$C \quad T \quad Ca \quad X \quad Cb$

A similar procedure is used to test the significance of yield data of the other treated plots. In the case of treated plots  $x$  and  $X$ , the data would be compared to the respective samples in plots  $ca$ ,  $cb$ ,  $Ca$ ,  $Cb$ , and so on.

In the case of treatments on large areas, where strips of treated and untreated crop alternate, the significance of yield data is also obtained by taking the difference between paired values directly. The number of paired samples required depends much on the evenness of the field and in some cases biometrically significant results may be obtained with but a few samples. In general, however, the more samples that are taken, the more reliable are the calculated values of the probable error, and it might be well to plan having at least twenty paired samples for each treated field.

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## A NEW STEM-END ROT OF POTATO<sup>1</sup>

BY W. R. FOSTER<sup>2</sup> AND H. S. MACLEOD<sup>3</sup>

### Abstract

A new disease of potato, a hard, dry, corky, stem-end rot with a sharply defined margin, is reported from the coastal area of British Columbia. Stem-end hard rot is the name suggested for this disease. A fungus, *Phomopsis tuberivora* Güssow and Foster, isolated from rot lesions, reproduced typical symptoms of the characteristic stem-end rot. The optimum temperature for the growth of the causal organism is between 20° and 25° C. The optimum hydrogen ion concentration for the growth is approximately 6.5.

Between 38° to 40° F. (3.34 to 4.45° C.) the usual storage temperature for potatoes, the disease makes little progress. Dipping the diseased potatoes in mercuric chloride, 1:1000, was not an effective control measure. Evidence of field experiments indicates that diseased tubers should not be used for planting purposes.

### Introduction

In October, 1930, Mr. H. S. MacLeod directed the senior author's attention to what appeared to be a new characteristic stem-end rot of tubers. It was observed in the following varieties: Irish Cobbler, Green Mountain, Early Ohio, Bliss Triumph, Nette Gem, Early Epicure, Columbia Russet and Early St. George, from the coastal area of British Columbia, Vancouver Island and Fraser Valley. This disease has not been reported from any sections of the Interior. Stem-end hard rot is proposed as the name for the disease.

### Symptoms of the Disease

The tubers become infected at the stem-end where a hard, dry, corky rot develops (Plate 1, Figs. 1 to 7) resulting in a slightly sunken circular lesion with a sharply defined margin. The general color of the lesion is wood brown (2), with a glistening margin of light neutral grey. On mature tubers the lesions vary in size from mere pin heads to those involving the whole tuber. Often many small immature tubers are found completely mummified early in the season. Small, brown or black raised bodies often break through the epidermis of the lesion. A typical longitudinal section through a lesion shows a dark, corky zone extending towards the centre of the inner medulla, producing a conical hard rot with a definite margin.

### Etiology

#### Isolation

In collaboration with Dr. H. T. Güssow the brown to black bodies breaking through the epidermis were determined to be the fruiting bodies of a hitherto undescribed species of *Phomopsis* to which the name *tuberivora* has been given (1).

#### Pathogenicity

Eight potatoes of each variety representing five tuber-groups were inoculated with mycelium from a single-spore culture of *Phomopsis tuberivora*, and

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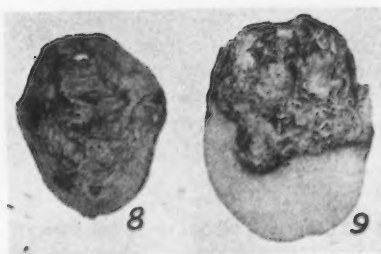
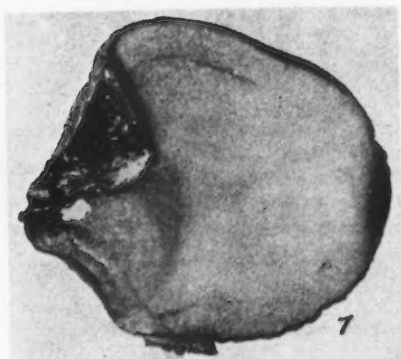
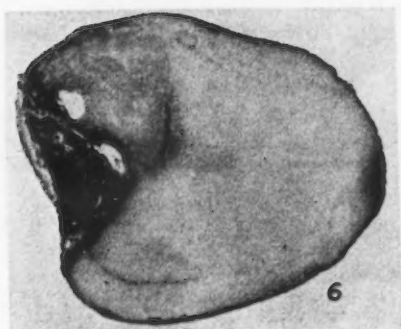
Contribution from the Provincial Plant Pathological Laboratory, Saanichton, British Columbia.

<sup>2</sup> Assistant Plant Pathologist, British Columbia Department of Agriculture.

<sup>3</sup> District Plant Disease Inspector, Dominion Department of Agriculture.



PLATE I



FIGS. 1-7. Stem-end hard rot of potato. FIGS. 8 AND 9. Potatoes inoculated with *Phomopsis tuberivora* Güssow and Foster.



typical symptoms of the disease obtained. Most of the inoculations were accomplished by wounding at the stem-end with an  $\frac{1}{8}$ -in. cork borer, followed by the insertion of mycelium from a single-spore culture under aseptic conditions. The wounds were protected from contamination by non-absorbent cotton. Later, it was found that wounding was not necessary. The data with reference to the inoculations are shown in Table I, and the characteristic symptoms obtained from artificial inoculation are illustrated in Plate I, Figs. 8 and 9. These developed in only four of the varieties, viz.: Irish Cobbler, Green Mountain, Early Ohio and Bliss Triumph, and not in Netted Gem. However, in the field, this variety proved to be susceptible, and in addition, Early Epicure, Columbia Russet and Early St. George.

TABLE I  
RESULTS OF INOCULATING FIVE VARIETIES OF POTATOES WITH *Phomopsis tuberivora*

Treatment	Group	Variety	Result
Check	Irish Cobbler	Irish Cobbler	No lesion
Inoculated	Irish Cobbler	Irish Cobbler	Typical lesion
Check	Burbank	Netted Gem	No lesion
Inoculated	Burbank	Netted Gem	No lesion
Check	Green Mountain	Green Mountain	No lesion
Inoculated	Green Mountain	Green Mountain	Typical lesion
Check	Ohio	Early Ohio	No lesion
Inoculated	Ohio	Early Ohio	Typical lesion
Check	Triumph	Bliss Triumph	No lesion
Inoculated	Triumph	Bliss Triumph	Typical lesion

### Environmental Factors

#### *Temperature Studies with Phomopsis tuberivora*

A culture of *Phomopsis tuberivora* was grown on potato-dextrose agar and exposed to temperatures ranging from 5° to 40° C. The results are shown in Table II.

TABLE II  
REACTION OF *Phomopsis tuberivora* TO TEMPERATURE

Temperature, °C.	5	10	15	20	25	30	35	40
Diameter*, mm.	4	7	33	47	60	12	3	1

\*Average diameter of three colonies incubated for three days.

The figures in Table II indicate that the optimum is between 20° and 25° C. These data support the authors' observation that the progress of the disease is very slow at proper storage temperature for potatoes, 38° to 40° F.

#### *Hydrogen Ion Studies*

The *Phomopsis tuberivora* was grown in petri dishes on media prepared by the method outlined by Webb and Fellows (3).

The hydrogen ion determinations were made immediately after the plates were poured, at temperatures of 15° to 16° C., by means of a hydroquinone potentiometer.

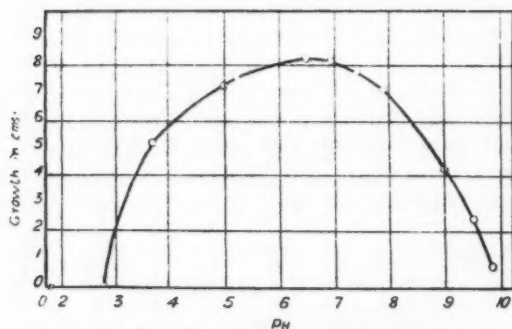


FIG. 10. Growth in centimetres of *Phomopsis tuberispora* at different hydrogen ion concentrations at 25° C.

The results of five days growth are shown in Table III and Fig. 10. Determinations of the pH at the end of the experiment showed that little change of the hydrogen ion concentration had occurred.

The results indicate that the optimum hydrogen ion concentration is approximately 6.5. In 1931 and 1932 the authors found tubers infected with stem-end hard rot in acid soil only.

TABLE III

REACTION OF *Phomopsis tuberispora* TO DIFFERENT HYDROGEN ION CONCENTRATIONS AT 25° C.

pH	2.8	3.7	5.0	5.2	6.5	6.9	7.4	7.9	9.0	9.5	9.8
Diameter,* mm.	0	52	72.5	75.7	82.5	81.8	77.7	71.3	43.2	24.2	6.5

\*Average diameter of three colonies for each pH.

### Control

Preliminary control investigations were carried on by Mr. H. S. MacLeod. Diseased and healthy Early Ohio potatoes selected from the same source, were immersed in mercuric chloride (1:1000) for 1½ hr. and planted in the field in uniform soil which had not been planted with potatoes for many years. The

TABLE IV

EFFECT OF TREATING EARLY OHIO POTATOES INFECTED WITH STEM-END HARD ROT WITH MERCURIC CHLORIDE (1:1000)

Treatment	Crops per acre, bushels		Diseased hills, %
	Healthy tubers	Diseased tubers	
Healthy tubers, not treated	312.1	0.2	2.5
Healthy tubers, treated	303.0	6.0	5.0
Diseased tubers, not treated	236.3	21.0	35.0
Diseased tubers, treated	156.0	63.0	80.0

first year's results shown in Table IV indicate that this method of control was not effective, as the percentage of diseased plants was higher from the treated than from the untreated seed. The bushels per acre (Table IV) are based on the yield of only one row of 40 hills, for each treatment. The planting of healthy tubers or sets with affected portions cut off gave a practical control in this experiment.

### Summary

1. A new stem-end rot disease of potato has been described.
2. *Phomopsis tuberivora* Güssow and Foster, isolated from rot lesions, reproduced typical symptoms of the characteristic stem-end rot.
3. Stem-end hard rot is the name suggested for this disease.
4. The optimum temperature for the growth of *Phomopsis tuberivora* is between 20° and 25° C.
5. At the storage temperature for potatoes, between 38° to 40° F. (3.34 to 4.45° C.), the disease makes little progress.
6. The optimum hydrogen ion concentration for growth of *Phomopsis tuberivora* is approximately 6.5.
7. The mercuric chloride treatment for potatoes was not an effective control measure.

### Acknowledgment

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## THE INFLUENCE OF HELMINTH PARASITISM ON THE ABUNDANCE OF THE SNOWSHOE RABBIT IN WESTERN CANADA<sup>1</sup>

By R. V. BOUGHTON<sup>2</sup>

### Abstract

The results are given of a survey of the helminth parasites of 420 rabbits (*Lepus americanus*) from the province of Manitoba. The survey yielded three species of Cestoda, two larval and one adult form, five species of Nematoda, two of which are regarded as new to science, an unidentified Acanthocephalan, and several species of the protozoan genus *Eimeria*. No Trematoda were found.

The biology and pathogenicity of the helminth parasites suggest that the three most dangerous parasites to the health of the rabbit population are *Nematodirus triangularis*, *Synhelocaulus leporis*, and *Eimeria* sp. A definite correlation between the percentage of rabbits infested by parasites and the meteorological conditions in the different soil areas of the province appears to exist.

It has been known for at least a century that *Lepus americanus*, the snowshoe rabbit of western Canada, is subject to periodic fluctuations in abundance, and that such fluctuations are paralleled by similar fluctuations in the abundance of animals which prey principally upon the snowshoe rabbit, such animals, for example, as the Canada lynx (*Lynx rufus* Gueldenstadt), the fox (*Vulpes fulva* Desmarest) and the coyote (*Canis latrans* Say).

Hewitt (7), from a study of the fur returns of the Hudson Bay Company, asserted that the periods of maximum abundance occurred in the following years: 1845, 1854, 1857, 1865, 1877, 1888, 1897, 1905 and 1914. This gives an average periodic cycle of 8.5 years, which approaches the prevailing popular idea of a seven year cycle for this animal. A maximum abundance however does not occur over the whole country in the same year; such abundance is usually regional in character and the period of general abundance may extend over several years.

Although these fluctuations in abundance of rabbits can be roughly forecasted, it would appear that between the years of abundance there are years of local scarcity. This was the view held by Seton (12) who collected many data in regard to the periods of increase and decrease of rabbits in different areas of western Canada. Seton places the following years as years of rabbit maxima in western Canada:

Lake of the Woods, 1856 (Hind).

Upper Assiniboine, 1857 (Hind).

Portage La Loche, 1875 (J. Macoun).

Shoal Lake and Stony Mountain, 1883-4 (J. H. Cadham).

Red River and Assiniboine Valley 1886-7.

Shoal Lake, 1893-4 (W. G. Tweddell).

Central Manitoba, 1894.

Northern British Columbia, 1872 (J. Macoun).

MacKenzie River Valley, 1903-4.

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Contribution from the Department of Zoology, University of Manitoba, Winnipeg, Manitoba, with financial assistance from the National Research Council of Canada supplemented by the resources of the Department of Zoology, University of Manitoba.

<sup>2</sup> Demonstrator in Zoology, University of Manitoba.

These fluctuations represent without doubt corresponding fluctuations in rabbit reproduction. The home range of the rabbit is restricted, in many cases to 30 or 40 acres (12), so that migrations of rabbits from area to area cannot be regarded as an important factor in the production of local variations in area population. It is more likely that the fluctuations are due to effects of epidemic disease. Such epidemics are usually associated with overcrowding, although not directly caused by it. The number of rabbits in an area usually increases over a period of years, and finally reaches a maximum; the year of maximum abundance is then followed by a period of epidemic disease, which diminishes enormously the rabbit population of the area. In all cases of observed epidemics among wild rabbits, no single disease has been found totally responsible for the epidemic. Most of the evidence concerning such epidemics is circumstantial, for, in some cases, dead rabbits are found in large numbers, while in other cases, although there is an appreciable decrease in the number of rabbits, few dead ones can be found.

Such evidence as exists with regard to epidemics among rabbits in western Canada is very scanty. Seton (12) records a number of examinations of rabbits that had apparently died during an epidemic. In a number of cases death was found to be due to gastric and intestinal catarrh, with small hemorrhages throughout the digestive canal, caused by roundworms. Another apparently died from a heavy infestation of *Multiceps coenurus*. Others have been reported as having died from enteritis, tuberculosis, pneumonia, and diarrhea. The data available seem, in fact, to indicate that rabbit epidemics are not due to a single infestation or disease, but to the total influence of a number of infestations and diseases, intensified to epidemic proportions by overcrowding.

Although many parasites of rabbits in North America have been recorded, there is very little evidence as to their incidence of infestation. No general helminthological survey of any species of rabbit has been hitherto attempted. D. Dilwyn John (10) made a survey of 516 rabbits in the Aberystwyth area in Wales, but his published data refer only to the incidence of infestation of the Cestodes. A list of the helminth parasites of *Lepus cuniculus* in Great Britain has also been recently published by the Imperial Bureau of Agricultural Parasitology (8).

The results put forward in this report are based upon an helminthological examination of 420 individuals of *Lepus americanus* Erxleben, carried out during the period December 1930 to December 1931, the material being obtained from 32 localities within the boundaries of the province of Manitoba.

### Material and Methods

The most important preliminary decision to be made with regard to the actual survey itself was the number of rabbits that should be examined, the intervals at which these examinations should take place, and the area to be covered. The ideal survey, of course, should consist of a monthly examination of a number of rabbits from a large number of localities representing the whole of the province. An alternative method is the monthly examination of as

many animals as possible from just one locality. When the area of the province of Manitoba, which occupies 251,832 square miles, is considered it is obvious that the difficulty and cost of transportation and the number of rabbits that would necessarily have to be examined render the ideal method impracticable. The alternative method is also unsuitable in so large an area, owing to the impossibility of selecting one locality topographically typical of the whole area.

Taking into consideration therefore the size of the province and the cost of collecting material over such a large area, it was considered best to restrict the survey to the southern third of the province, an area of approximately 83,000 square miles, and to make two or three examinations from a limited number of locations during the period of the survey.

During the course of the survey dependence had to be placed upon people in various parts of the province for material; in some cases however between periods of examination some of these people moved, while others neglected to send in more than one shipment. As a result the incidence of infestation of a particular area has in many cases been determined for only one period of the year.

During the summer months rabbits could not be sent in for examination, and it was necessary to spend considerable time in the field during that period. In considering the incidence of infestation between different localities it is necessary to base the results upon samples of approximate equality.

The age of only those rabbits that had been born during the summer of the survey could be determined with any degree of accuracy. All animals older than six months were considered as adults.

The autopsy consisted of a systematic search of all the organs for helminth parasites. The examination of the digestive tract was facilitated by forcing tap water through the intestinal region of the gut and decanting the washed-out debris. In the centrifugal examination of fecal material for eggs, a solution of three parts of cane sugar to two parts of water was used. In such a solution eggs and protozoan cysts can be kept on a slide for some months in excellent condition for examination.

Parasitic infestation could not be determined with certainty during the winter by means of fecal tests, because egg laying is then at a minimum and in some cases does not occur at all. This is particularly the case with *Passalurus nonanulatus*, a roundworm of the large intestine.

In the examination the material was removed as soon as possible after the rabbits were killed. Cestodes were washed in water, stretched upon a glass plate and painted with a fixing solution (10% formalin, acetic sublimate, or Zenker's solution) raised to a temperature of 80°C. Another method of fixing cestodes was to flood them, while *in situ*, with water at a temperature of 70°C. By either method the cestodes were killed in a fully extended condition. The material was preserved in either 5% formalin or 70% ethyl alcohol. The nematodes were fixed in 70% alcohol and 5% glycerol raised to the boiling point.

The best stain for the cestode material was cochineal (one part to five parts of water); differentiation was not necessary. For the nematode material, Erlich's hematoxylin was the most suitable stain. The cestodes were cleared in beechwood creosote, while the nematodes were examined in glycerol.

Cultivation experiments were carried out with *Nematodirus triangularis* and *Synthetocaulus leporis*. Attempts were made with unmodified feces on layers of filter paper. All the conditions appeared favorable for development, but in the case of *Nematodirus triangularis* the results were entirely negative; in the case of *Synthetocaulus leporis* however free larval stages were easily procured; the eggs hatched in the water before the fecal material could be emulsified sufficiently to centrifuge. To obtain a photomicrograph it was necessary to treat the feces with full strength formalin, and even this treatment only retarded egg development, hatching taking place within 12 hr.

In the case of *Nematodirus triangularis* ten other cultures in charcoal and humus were isolated after different periods of time varying up to 15 days, but all failed to yield a single larva. Later, unmodified feces were left covered with water, the water was allowed to evaporate, and the mass of fecal material was left to dry for two days. On the fifth day water was added, and a small percentage of the eggs were found to contain fully developed actively moving embryos. Unfortunately the amount of fecal material in this case was not sufficient to determine whether the eggs would hatch, and time did not permit of further experiments. The fecal material was obtained from wild rabbits kept in captivity. The final experiments were carried on during February, and it is possible that those eggs which are laid during the winter do not hatch; to determine this point further experiments will be necessary.

Sufficient experiments were performed, however, to indicate that a free-living larval stage exists in the case of *Synthetocaulus leporis*, and that a similar stage probably exists in the case of *Nematodirus triangularis*. The fact that the eggs of *Synthetocaulus leporis* develop and hatch within such a short time probably accounts for the high percentage of host infestation, and the greater number in the individual host. It is quite possible that the stage of infestation is reached in a much shorter time than in the case of *Nematodirus triangularis*, so that wet or moist conditions would be required only for a short time, in order to permit egg development, hatching and for host infestation to take place.

### The Helminth Fauna

The helminths recorded from rabbits, in most cases, are cosmopolitan in distribution; a few however are local. The helminths recorded in the present paper comprise three species of Cestoda, five species of Nematoda, and an unidentified Acanthocephalan. No Trematoda were found. The protozoan genus *Eimeria* was represented by several species. The helminths found may be listed as follows:—

#### Cestoda

Fam. Anoplocephalidae. *Cittotaenia pectinata americana*. (Goeze 1782 *partim*, Riehm 1881, Stiles and Hassel 1896)

Fam. Taeniidae.	<i>Taenia pisiformis</i> . sp. larva. (Bloch 1780)
	<i>Multiceps serialis</i> . sp. larva. (Gervais 1847)
Nematoda	
Fam. Rhabdiasidae.	<i>Strongyloides papillosus</i> . (Wedl. 1856)
Fam. Trichuridae.	<i>Trichuris leporis</i> . (Froelich. 1789)
Fam. Trichostrongylidae.	<i>Nematodirus triangularis</i> n. sp. <i>Trichostrongylus</i> . sp.
Fam. Metastrongylidae.	<i>Synthetocaulus leporis</i> n. sp.
Fam. Oxyuridae.	<i>Passalurus nonanulatus</i> (Skinker 1931)

The results of the survey are summed up in Table I. In determining the incidence of infestation, it was thought best, in order to obtain the average infestation, to consider, as nearly as possible, equal numbers of rabbits from the different localities. This was done for two reasons: (a) due to the possible effect of the various factors of the environment; and (b) because the percentage of infestation would necessarily be reduced during the breeding season due to the sudden increase in numbers. In other cases the parasites were not found until the survey had been partly completed and, as a result, only generalized statements can be made. The fact that the large majority of the rabbits were frozen when received made it difficult in some cases to detect some of the parasites.

TABLE I  
RELATIVE FREQUENCY OF DIFFERENT PARASITES

Parasite	No. examined	No. infested	% Infested
<i>Cittolaenia pectinata</i>	388 (ad.)	1	0.26
<i>Cittolaenia pectinata</i>	32	32	100
<i>Taenia pisiformis</i>	288	42	14.7
<i>Multiceps serialis</i>	288	45	15.6
<i>Strongyloides papillosus</i>	388 "	3	0.75
<i>Trichuris leporis</i>	288	29	10.07
<i>Nematodirus triangularis</i> and <i>Trichostrongylus</i>	288	73	25.35
<i>Synthetocaulus leporis</i>	30	25	83.3
<i>Passalurus nonanulatus</i>	288	31	10.7
<i>Acanthocephalid</i>	388	2	0.50
<i>Eimeria</i>	50	40	80

The rabbits were caught during four definite periods, the first from Dec. 15, 1930 to Jan. 20, 1931, the second from Mar. 1 to Apr. 1, 1931, the third from July 15 to Aug. 20, 1931, and the fourth from Oct. 20 to Dec. 30, 1931.

A summary of the infestation, during the three periods, of those parasites for which sufficient data are available is given in Table II. In the case of the



nematodes there appears to be a large decrease in the percentage of infestation in the third period, in contrast to the first period, while in the case of the cestodes there appears to be a slight increase.

TABLE II  
COMPARISON OF INFESTATION DURING THREE PERIODS OF THE SURVEY

Parasites	Period	No. examined	No. infested	% infested	No. of males	% Males	% Females
<i>Nematodirus triangularis</i> and <i>Trichostrongylus</i>	Dec. 1930	164	47	28.6	31	65.9	34.1
	Apr. 1931	59	17	28.8	11	64.7	35.3
	Dec. 1931	65	8	12.3	5	62.5	36.5
<i>Trichuris leporis</i>	Dec. 1930	164	20	12.2	13	60	40
	Apr. 1931	59	6	10.1	4	66.6	33.4
	Dec. 1931	65	4	6.1	3	75	25
<i>Passalurus nonanulatus</i>	Dec. 1930	164	15	9.15	9	66.6	33.4
	Apr. 1931	59	11	18.6	8	72.7	27.3
	Dec. 1931	65	5	7.7	2	40	60
<i>Taenia pisiformis</i>	Dec. 1930	164	22	13.4	14	63.6	36.4
	Apr. 1931	59	9	14.2	6	66.6	33.4
	Dec. 1931	65	11	16.9	6	54.5	46.5
<i>Multiceps serialis</i>	Dec. 1930	164	21	12.2	12	57.1	42.9
	Apr. 1931	59	12	20.3	6	50	50
	Dec. 1931	65	12	13.4	9	75	25

NOTE:—Number of males examined—164 equals 56.9%; Number of females examined—124 equals 42.1%.

*Cittotaenia pectinata americana*

(Goeze 1782 *partim*; Riehm 1881; Stiles and Hassel 1896.) See Fig. 1.

*Habitat.* Small intestine of *Lepus americanus*, from the province of Manitoba. Common in young individuals. Life history unknown.

*Specific diagnosis.* Cestodes of large size, maximum length being 220 mm., and 7 mm. in breadth. Segmentation beginning almost immediately back of the head, the proglottids rapidly becoming distinct and always much broader than long. Scolex provided with four shallow acetabula. The *anlagen* of the genital organs appear early. Testes appear about 6 mm. back of the head; genital pores double, in the posterior half of the margin. Testes about 0.64 mm. in diameter, numerous, numbering about 112, and confined to the distal half of the segment, posterior to the uterus, and extend across the entire median field passing the ovary on each side of the longitudinal canals, cirrus pouch about 1 mm. in length, extending some distance median of the longitudinal canals.

Ovary, shell gland and vitellogene gland about 1 mm. from the lateral margin. A common transverse uterus to both ovaries. Cirrus pouch, vagina and uterus pass from the median field into the lateral field dorsally of the longitudinal canals and nerves. Ova about 78  $\mu$  in diameter (Plate I, Fig. 1).



*Taenia pisiformis*. sp. larva

(Bloch 1780)

This metacestode is often called *Cysticercus pisiformis* and occurs commonly in the liver and abdominal cavity of the rabbit. Number of hooks on the rostellum 34 to 48. Length of the large hooks 225 to 294  $\mu$ . Length of the small hooks 132 to 177  $\mu$ .

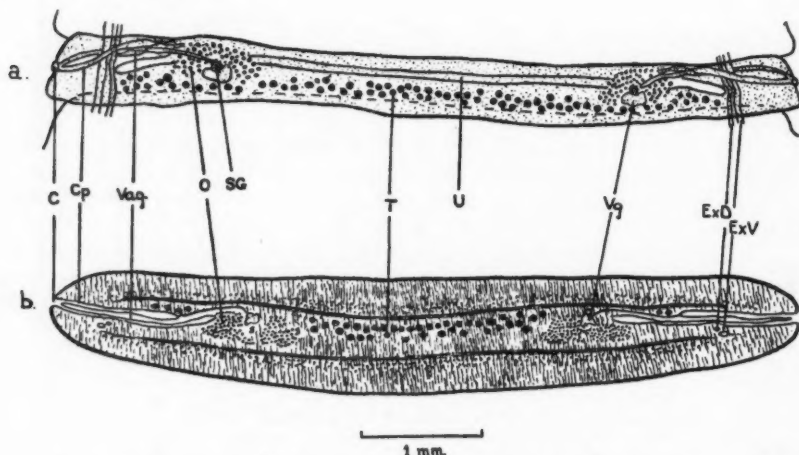


FIG. 1. *Cillotaenia pectinata americana*, mature proglottis; a, dorsal view; b, transverse section; C, genital cloaca; Cp, cirrus pouch; ExD, dorsal excretory vessel; ExV, ventral excretory vessel; O, ovary; SG, shell gland; T, testes; U, uterus; Vag, vagina; Vg, vitelline gland.

*Multiceps serialis*. sp. larva

(Gervais 1848)

The cystic form of this cestode is often called *Multiceps coenurus*, and occurs commonly in the connective tissue, especially the subcutaneous tissue. Number of hooks 26 to 32. Length of the large hooks 135 to 175  $\mu$ . Length of the small hooks 78 to 120  $\mu$ .

*Strongyloides papillosus*

(Wedl. 1856; Ransom 1911) See Fig. 2.

**Specific diagnosis.** Parasitic generation,—length 3.5 to 6 mm.; thickness 50 to 60  $\mu$ . Body filiform, posterior end of the body diminished in size backward beginning some distance in front of the anus, and terminating in a slight tapering tail with rounded tip. Anus 55 to 70  $\mu$  from the posterior end. Vulva, a transverse slit with rather salient lips situated 1.6 to 2 mm. from the posterior end of the body. Eggs ellipsoid, with very thin shells 20 by 40  $\mu$  to 60 by 25  $\mu$ . Not more than a dozen fully formed eggs present in the two uteri at any one time.

**Location.** Large intestine.

**Localities.** Europe, United States, South America, Canada.

**Hosts.** *Lepus cuniculus*, *Mus decumanus*, *Lepus americanus*.

*Trichuris leporis*

(Froelich 1789; Hall 1916) See Figs. 3, 4.

*Specific diagnosis.* Head 17 to 20  $\mu$  in diameter, and extending to below the vagina. On each side of the bacillary band an area of delicate cuticular plaques.

*Male:* 29 to 32 mm. long, with a maximum diameter of about 500  $\mu$ . Ratio of the length of the anterior esophageal portion of the body to the length of the posterior portion is 3:2. Spicule 2.88 mm. long, with a diameter of about 8 to 10  $\mu$ .

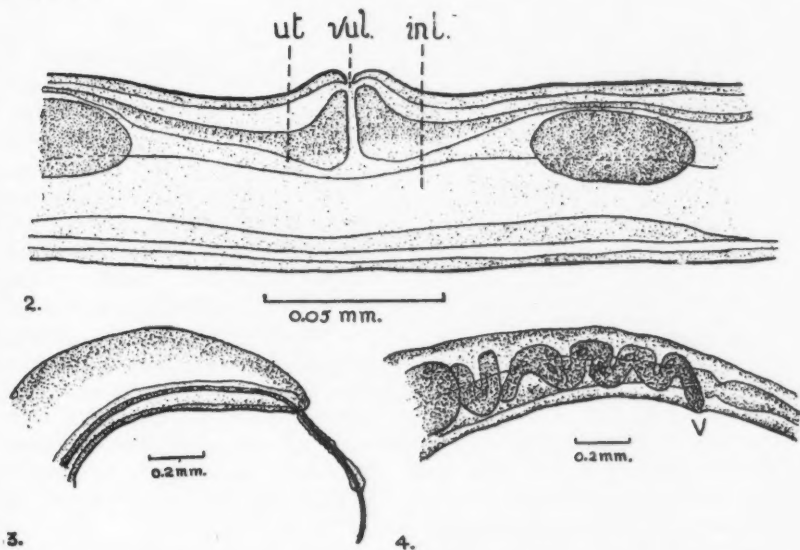


FIG. 2. *Strongyloides papillosus*. Body in region of vulva. int, intestine; ut, uterus; vul, vulva. FIG. 3. *Trichuris leporis*. Posterior extremity of male, showing sheath and spicule. FIG. 4. *Trichuris leporis*. Region of female showing pocketing in vagina. v, vulva.

*Female:* 24.5 to 32 mm. long, with a maximum diameter of about 910  $\mu$ . Ratio of the length of the anterior esophageal portion of the body to the posterior portion 2:1. Vagina appears to comprise a series of pouches or pockets. Eggs 66 to 70  $\mu$  long, including the opercular plugs, by 26 to 30  $\mu$  in breadth. (Plate I, Fig. 1).

*Host habitat.* Large intestine.

*Hosts.* *Oryctolagus cuniculus* (*Lepus cuniculus domesticus* L. c. *ferus*) *Lepus europaeus* (*Lepus timidus*), *Lepus timidus* (*Lepus variabilis*), *Sylvilagus floridanus*, *Sylvilagus floridanus mallurus*. *Citellus citellus* (*Arctomys citellus*, *Spermophilus citellus*), *Lepus americanus*.

*Localities.* Germany, France, Switzerland, Austria, Italy, United States, Canada.

*Nematodirus triangularis*. n. sp.

See Fig. 5.

**Specific diagnosis.** Slender worms of small size. Inflated cuticle of neck asymmetrical, and conspicuously striated.

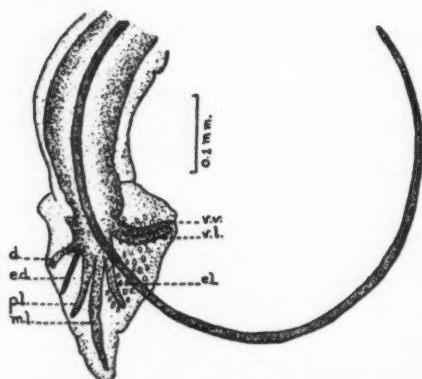


FIG. 5. *Nematodirus triangularis*. Bursa from the right side. d., dorsal ray; e.d., externo-dorsal ray; e.l., externo-lateral ray; m.l., medio-lateral; p.l., postero-lateral; v.l., ventro-lateral ray; v.v., ventro-ventral ray.

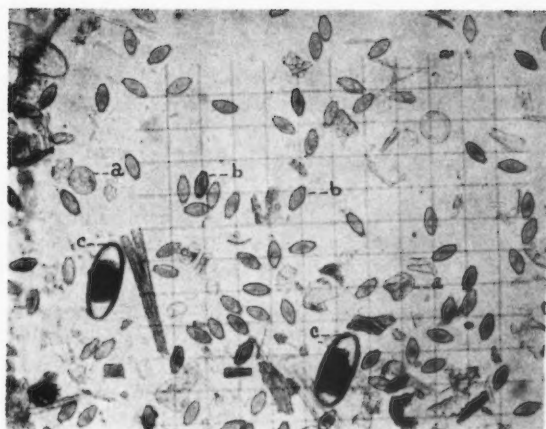
**Male:** 8 to 11 mm. long with a maximum diameter of from 88 to 115  $\mu$ . Esophagus 400 to 500  $\mu$  in length. Bursa well expanded, its length 260  $\mu$  greater than its breadth 185  $\mu$ . Ventral lobes set off from the lateral lobes by a distinct notch. Dorsal ray bifurcated to about one-fifth its length. Externodorsal rays long and very slender, about midway between the dorsal ray and the postero-lateral ray. Postero-lateral and the externo-lateral ray much shorter and curving sharply away from the medio-lateral ray. Latero-ventral and ventro-ventral rays in contact for their whole length, curved backward and ending close to the

bursal margin. These rays are much more slender than the lateral rays, but much thicker than the dorsal rays. Their length is about one-half that of the medio-lateral rays. Bosses are numerous and small. Spicules deep brown in color, 1.4 to 1.7 mm. long, united for the greater part of their length, and showing distinct striations on the proximal half. Tip of the spicule curved ventrally and ending in a sharp point.

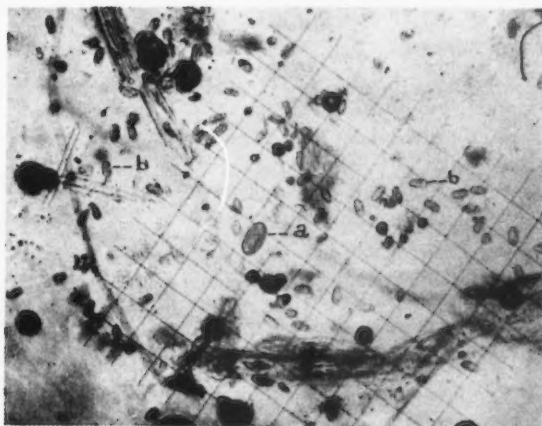
**Female:** 9 to 13 mm. in length with a maximum diameter of 100 to 160  $\mu$  at the vulva. Diameter moderately reduced behind the vulva. Head diameter 35 to 40  $\mu$  exclusive of the inflated cuticle, latter well developed reaching a diameter of 50 to 70  $\mu$ . Esophagus 450 to 600  $\mu$  in length. Tip of the tail truncated and provided with the usual bristle-like process. Anus 70 to 80  $\mu$  from the truncated end of the body. Vulva, a transverse slit in the posterior third of the body. Long, oval eggs measuring 175 to 195  $\mu$  by 75 to 85  $\mu$  (Plate I, Fig. 1) with thin smooth shell of uniform thickness, in various stages of development from six-celled to the morula stage.

This form seems to come nearest in structure to the species *flicollis* (11), which it resembles in general bursal characteristics, in the position of the vulva and of the anus. The male differs however from *flicollis*, in the shape of the bursa, which is definitely triangular, and is sufficient to distinguish the males from any other species of the genus, in the details of the arrangement and relative size of the bursal rays, and in the length and thickness of the body. The writer is therefore of the opinion that this material represents a hitherto unrecorded species, and the species name *triangularis* is suggested.

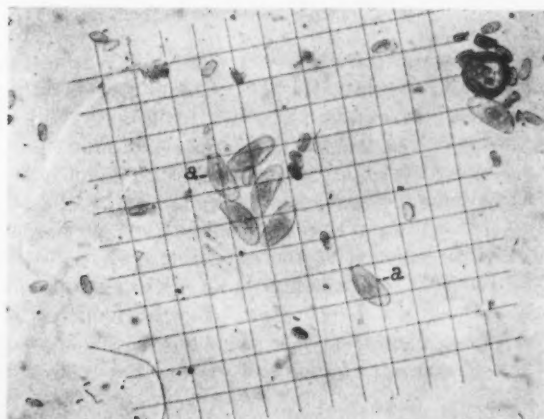
PLATE I



(1) a. Eggs of *Cillotaenia pectinata americana*. b. Eggs of *Trichuris leporis*. c. Eggs of *Nematodirus triangularis*.



(2) a. Eggs of *Synthetocaulus leporis*. b. Cysts of *Eimeria* sp.



(3) a. Eggs of *Passalurus nonanulatus*.



*Type host.* Snowshoe rabbit (*Lepus americanus*).

*Type locality.* Southwestern part of the province of Manitoba.

*Location.* Duodenum.

*Trichostrongylus* sp.

(Looss 1905)

This parasite could be identified only as to genus, which is also doubtful, due to the limited amount of material available, and its poor state of preservation

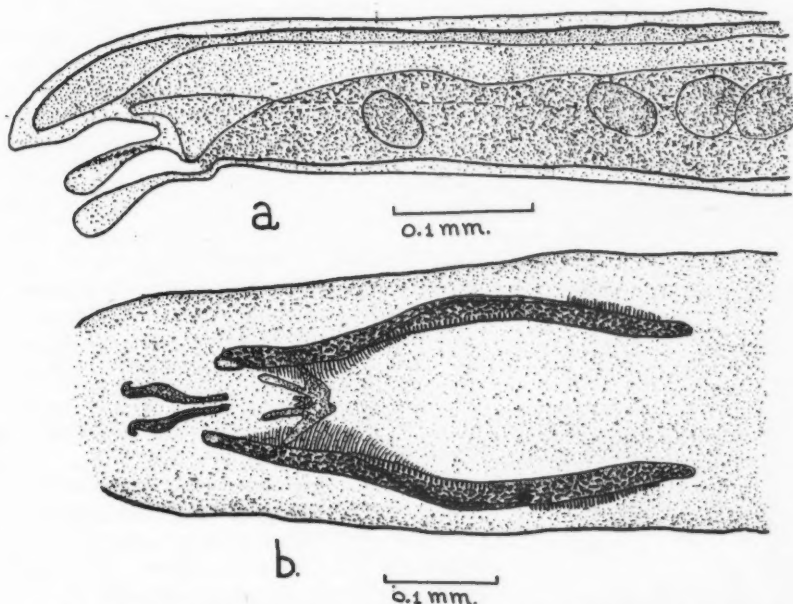


FIG. 6. *Synthetocaulus leporis*. a., posterior extremity of female; b., posterior extremity of the male, showing spicules.

*Synthetocaulus leporis*. n. sp.

See Fig. 6.

*Specific diagnosis.* Body filiform. Anterior extremity attenuated and head obtuse. Head with three lips and with six very small circumoral papillae. The slender esophagus is slightly dilated posteriorly. Intestine is dark brown.

*Male:* 23 to 28 mm. long and 154 to 176  $\mu$  thick. The esophagus is 276 to 330  $\mu$  long. The small bursa is characteristic of the genus (5). The spicules are 260 to 305  $\mu$  long, they are flat, somewhat chitinous rods, broader at the proximal end, and the body of the spicules is marked with a distinct marbling. They are provided with chitinous lateral lamellae, in which are chitinous rods set at right angles to the longitudinal axis of the spicule. The rods are thicker in the proximal portion of the spicule, in the distal portion the lamellae become wider, and the rods in them become thinner, so that on the distal end they are perceptible only as very fine lines on the thin lateral lamellae. The



lamellae are directed toward one another distally, but curve gradually around the spicule proximally. With the spicules retracted, the unpaired accessory structure lies between them in their distal portion. Its general outline is



FIG. 7. *Passalurus nonanulatus*. Posterior end of male, lateral view.

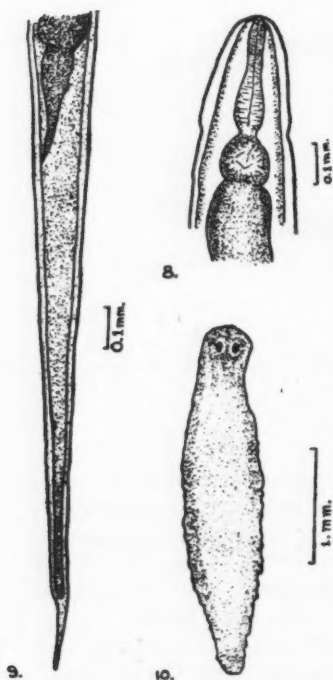


Fig. 8. *Passalurus nonanulatus*. Anterior end of female. FIG. 9. *Passalurus nonanulatus*. Posterior end of female. FIG. 10. *Cittolaenia pectinata americana*. Small immature form.

chevron-shaped with the point of the chevron directed anteriorly, and consists of six to eight sickle-shaped chitinous structures projecting from a centre. The paired accessory structures are located in the bursal region, and are approximately parallel structures 68 to 84  $\mu$  long. These structures consist of a broad slightly bent stem, broader toward the distal end, where they curve postero-ventrally.

*Female*: 25 to 40 mm. long and 154 to 242  $\mu$  thick. The tail is bluntly truncated and the anus is very close to the tip of the tail. The vulva is just anterior to the anus and is 135 to 194  $\mu$  from the tip of the tail. The vagina is 1.9 to 2.4 mm. long. Anterior and posterior of the vagina two club-shaped organs occur, which apparently act as ovi-positors and are 90 to 110  $\mu$  long. There are two convergent uteri. Eggs (Plate I, Fig. 2) are elliptical, very thin shelled, 65 to 75  $\mu$  long and 40 to 50  $\mu$  thick. They show no trace of segmentation at oviposition.

This species of *Synthetocaulus* seems to come nearest in structure to the species *pulmonalis* (5), which it resembles in general bursal characteristics and size of the vagina. The male differs however in the shape and size of the spicules and accessory structures, the length and thickness of the body and the short esophagus. The female differs in its shorter and more slender body, and the size of the eggs, and in the presence of the two club-shaped organs; the latter characteristic is sufficient to distinguish the female from any other species of the genus. The writer is of the opinion that this material represents a species hitherto unrecorded and the specific name *leporis* is suggested for it.

*Type host*. Snowshoe rabbit (*Lepus americanus*).

*Type locality*. Southern portion of the province of Manitoba.

*Location*. Bronchi, bronchioles, and pulmonary parenchyma.

*Passalurus nonanulatus*

(Skinker 1931). See Figs. 7, 8, 9.

**Male:** 3.4 to 4.1 mm. long with a maximum width of about 272  $\mu$ . The entire esophagus from 396 to 400  $\mu$  long. The bulbar region about 114 to 122  $\mu$  long. The spicules are about 115  $\mu$  long.

**Female:** 7.2 to 8 mm. long with a maximum diameter of 400  $\mu$ . The esophagus measures 525 to 555  $\mu$  in length, the bulb alone being 144 to 160  $\mu$  long, and 144 to 176  $\mu$  wide. The anus is situated about 1.6 mm. from the posterior end. The slender portion of the tail is 152  $\mu$  long. The eggs (Plate I, Fig. 3) are thin-shelled and 90 to 132  $\mu$  long and about 60  $\mu$  wide.

**Hosts.** Snowshoe rabbit (*Lepus americanus*), coyote (*Canis lestes*).

**Distribution.** United States (Cheboygan County, Mich., and Olympia, Wash.); Canada (province of Manitoba).

**Location.** Large intestine.

Skinker (13) gives the location of this species as the small intestine. The writer, out of a total of 288 rabbits examined, has always found them in the large intestine.

## Family Eimeriidae

Reference may be made to the occurrence of oocysts of *Eimeria* in the intestine. There appear to be at least two species present. Oocysts varying from 36 to 52  $\mu$  in length by 24 to 27  $\mu$  in breadth were found to be the most common. They are ellipsoidal or ovoid in shape, and of a yellowish color. Many of the oocysts show flattening at the micropyle end. A second type found was exceptionally constant in size, measuring 15  $\mu$  in length by 11  $\mu$  in breadth. The oocysts are almost colorless, elliptical in shape, and there is no flattening at the micropyle end (Plate I, Fig. 2).

Possibly the first form represents *Eimeria stiedae* (Lindeman 1865) and the second form represents *Eimeria perforans* (Leuckart 1879).

**The Biology and Pathogenicity of the Leporine Parasites**

Although numerous genera of cestode parasites such as, for example, *Cittotaenia*, *Thysanosoma*, *Stilesia*, and *Moniezia*, are parasites in herbivorous animals, in no case has the life history been described. While the present paper does not deal to any extent with the life history of *Cittotaenia*, with the exception of direct feeding experiments, the occurrence and numbers of the cestodes found may help in determining whether or not an intermediate host occurs.

A number of outstanding features have been noticed with regard to the infestation of rabbits with *Cittotaenia*. One is the similarity in the occurrence of *Cittotaenia*, with that of *Moniezia* in the sheep, which has been dealt with to some extent by R. W. Jenkins (1924). Another important feature is the early age at which infestation occurs. Young rabbits from three to five weeks old were found, at autopsy, to be infested with from three to fifteen immature cestodes; all rabbits caught during the third week in July, and which had been among the first litter, probably in May, were found to be infested, the cestodes varying in development from immature forms a few mm. long (Fig. 10) to

mature forms 220 mm. long. Infestation must take place while the young are still on a milk diet or immediately after the change to the herbivorous diet.

The majority of infestations take place from the time the rabbits are three weeks old until they are two months old, but infestation is not confined to this period; immature forms only a few mm. long were found in rabbits that, as far as could be determined, were six months old when caught on October 25. As the first litters are born about the first of May, this period of infestation extends roughly from June 1 to November 1. The period of maximum infestation appears to occur from June 1 to August 1. This period was determined when the maximum number of immature forms were found, and not necessarily when the maximum number of cestodes were found.

Another outstanding feature with regard to the occurrence of *Cittotaenia* is the sudden disappearance of the cestodes in young rabbits during the month of November. From June 1 to about November the incidence in young rabbits is 100%; within a period of three weeks, from November 1 to about November 21 the cestodes are almost totally lost.

Of the 420 rabbits examined, 388 were adults in which infestation was only 0.26%. The rabbits in which the cestodes are lost acquire an immunity which is retained throughout life, because all adult rabbits examined during the time the young rabbits were infested were found to be uninfested. This condition was also supported by examinations during the summer of 1932.

It would appear as if the elimination of the cestodes was due to a change of diet, from soft grass foods to that of bark in the late summer, which takes place about November 1. The adhesive organs of *Cittotaenia*, which consist of four acetabula, are very weak, and it is possible that the mechanical effects due to the movement of the bark cause the cestodes to pass out



FIG. 11. Figure shows space occupied by an immature form of *Cittotaenia pectinata americana* in the ileum of a rabbit only a few weeks old.

of the host. The ileum has a very small lumen and a number of worms are often found together, or in some cases a single worm is found folded upon itself a number of times (Fig. 11); in either case the gut is often distended in those particular regions. When such a condition exists the worms constitute a serious obstruction to the passage of food material, especially if the infestation is heavy; with the change to a diet of bark the worms pass out of the host.

To determine if this were the real cause of the loss of the worms, a wild rabbit, in which infestation was indicated by the presence of "eggs" in the

fecal material, was kept in captivity from November 1 until February 15, when it died. During this period it was fed upon only a soft diet, and did not pass any worms; at autopsy five mature cestodes were found. Unfortunately these results are based upon a single observation, without a control, which was not secured due to the fact that the worms are lost within such a short time; nevertheless it appears from this experiment and observations in the field that the loss of the worms is due to the mechanical effects caused by the movement of the bark.

*Cittotaenia* infestation appears to be general all over the province of Manitoba. The topographical characteristics of the area cannot be correlated with the incidence of infestation. As far as can be determined the types of soil, type of vegetation, rainfall or snowfall do not appear to be factors influencing either the percentage of rabbits infested or the number of cestodes found in the individuals. In this respect the cestodes differ from the nematodes.

With regard to the life history two hypotheses exist: (a) some authorities suggest that there is direct infestation without an intermediate host; and (b) other authorities assume that the life cycle is indirect, with the existence of an intermediate host. The latter hypothesis is in accordance with the life history of the majority of cestodes. Direct feeding experiments were tried by feeding rabbits with ripe proglottids that had been kept in water for a number of months, and with "eggs" found in the fecal material. The results were entirely negative.

With regard to an intermediate host three possibilities exist:—

1. The intermediate host may be very common during the period of maximum infestation.
2. The intermediate host may not be common, but may harbor a large number of larval forms.
3. The intermediate host may not be common, but the larval form may be of a multiple type.

It is possible that all three conditions exist. If an intermediate host exists the first condition must exist, because infestation is uniform. If only conditions two and three exist it would be more likely that infestation would be patchy, and that the numbers found in the individual would be large. The second condition may exist but this hardly seems possible, since in this case one would expect to find the worms all of the same age. This is not so; forms are found from a few mm. up to 220 mm. in length. The number found in any one individual has never exceeded 15; in this case it differs from the numbers found in the sheep in which Jenkins (9) has recorded 230 cestodes in the same individual.

The conclusions which may be made in regard to the life history are:—

1. Direct feeding experiments gave negative results.
2. The fact that young rabbits become infested about three weeks after birth, and that infestation is 100%, appears to support the view that an intermediate host exists. With an infestation of only 0.26% in the adults it hardly seems possible that infestation could otherwise spread so rapidly and uniformly.

3. Infestation takes place from June 1 to November 1.
4. The topographical characteristics of the province give no clue to the life history.
5. Examinations of stomach contents of rabbits which harbored a number of very small cestodes in the small intestine gave negative results.

The pathological effects produced by *Cittotaenia pectinata* in adult rabbits can be entirely disregarded since infestation occurs only in 0.26% of those examined. Although infestation in young rabbits is 100% it is of little importance in this case as the cestodes are lost in the fall.

#### *Taenia pisiformis*

The larval form of *Taenia pisiformis* of dogs is *Cysticercus pisiformis*; this larval form is usually found in the liver as transparent vesicles, the mesentery, and organs of the body cavity of rabbits. In a few cases the cysts were surrounded by a large mass of calcareous material, lying loose in the body cavity. In two cases partly developed forms were found in the small intestine of the rabbit, these probably represented forms which had failed to bore through the intestinal wall, but instead had proceeded to develop and begin segmentation. Infestation amounted to 14.7%; the maximum number of cysts was 106, the average number being 20.

#### *Multiceps serialis*

The larval form of *Multiceps serialis* is usually called *Multiceps coenurus*. These larval forms develop in the rabbit in the connective tissue, under the skin and between the muscles, and are characterized by the production of daughter bladders, which in turn develop numerous scolices. The percentage of infestation amounted to 15.6%, the maximum number of cysts being 14, and varied in size from  $\frac{1}{2}$  to  $2\frac{1}{2}$  in. in diameter, with a maximum length of 4 in. In four cases cysts were found on the heart, the largest being an inch in diameter. These cysts may have been the larval form of *Multiceps packii* (2) but it was impossible to determine this from the size and shape of the hooks. In one case the lungs were infested by this parasite.

This parasite can no doubt cause sufficient pathological effects to produce death; however the number of cysts or the size of the cysts would have to be considerable. A heavy infestation not only hinders the rabbit in its movements, but also may retard or completely prevent the change in the color of the fur, making it an easy prey to its enemies. Reporting on a specimen that had died, Dr. W. Reid Blair of the New York Zoological Park states\*, "Death was due to a generalized infection with tapeworm cysts. These cysts are present in enormous numbers in practically all tissues of the body, the liver, mesentery, diaphragm, spleen, and pectoral muscles being most involved. A multilobular cyst situated over the ribs on the left side was completely encapsulated by the superficial muscles. This cyst contained besides four ounces of clear fluid, about three hundred heads of *Taenia* (mature) every one of which is fully capable, under favorable conditions, of developing into a mature tapeworm".

\*See Reference (12).



Coming now to the biology of the nematode parasites found, it is clear that *Strongyloides papillosus* and the *Acanthocephalid* worm occur so seldom as to have no possible influence on host abundance. *Strongyloides papillosus* was found in only 0.75% of the rabbits, and the small size and number found in each infested host (usually four, and in one case ten) indicates that unless there is an enormous increase in years of epidemic, this species is of little importance. The remaining species demand a more detailed discussion.

*Nematodirus triangularis* and *Trichostrongylus*

These small roundworms are easily recognizable. They are the only roundworms to be found in the small intestine and both male and female are usually found coiled each in a spiral. The worms occur in 25.35% of the rabbits. To make any definite statements with regard to the pathological effects of these worms upon their host is rather difficult, but it is well known that small size in nematodes does not necessarily imply non-pathogenicity. Recent investigations have shown that the members of the superfamily Strongyloidea produce hemolytic and cytolytic toxins (6). Although caution must be used in comparing the effects produced by closely related species of parasites it is possible that the effects produced by *Nematodirus* and *Trichostrongylus* may be similar to those produced by *Ankylostoma* infestation in man, in which the adult worms, by tearing bits of the mucosa from the intestine, produce small hemorrhages, the bleeding being maintained by the excretion of a hemolytic toxin. The worms constantly change their position, and when the numbers are great the loss of blood may be considerable. Providing the numbers are great enough, the total effect produced by the hookworm would be to produce an anemic animal, often retarded in physical and mental development.

Since we are concerned mainly with the lowering of the resistance of the host, the frequency of the worms in the rabbits is of importance. The numbers in any individual never exceeded 60 worms. This number would probably not produce fatal effects. The factors affecting the percentage of infestation and the number of worms found in the individual will be discussed in a later part of the paper.

*Trichuris leporis*

*Trichuris* is generally known as the whipworm, and occurs in the large intestine. Ten per cent of the rabbits were found to be infested, but never in large numbers, 29 being the maximum number, so that they could hardly be of any pathological importance, unless the incidence is greatly increased during epidemic years.

*Synthesocaulus leporis*

This species occurs in the bronchioles and pulmonary parenchyma. The percentage of infestation has not been determined for this worm, because infestation was rather difficult to detect in tissue that had been frozen; however, the percentage is undoubtedly very high since 25 out of 30 freshly killed rabbits examined were infested. The number of individuals present in the lungs has not been determined but 50 or 60 worms were not uncommon in one lobe of the



lung. Infestation is indicated externally by grayish patches on the lungs, indicating the areas in which the worms are localized. The pathological effects produced by infestation with this genus have been summarized by Hall (5) who reviews a study made by Doctor (1907). Hall states: "He finds the initial stages characterized by bronchitis and peribronchitis. Secondly there occurs bronchiectasis, collapse of the aveolar groups, and atelectasis. The changes follow a pneumonic process which is different from others in that it is characterized by extended epithelial desquamation, and a diffuse, progressive course from which it may be known as desquamative pneumonia. This may heal by a regeneration of the denuded epithelium accompanied by hyperemia. If the worm invasion was massive, or if weak respiration or absence of expectoration hinders the elimination of the exudate due to the parasite, there follows a tissue necrosis by progressive caseation, which may show a caseous bronchitis and caseous pneumonia. This may determine extensive destruction of lung tissue or induration." Since this parasite, even at present, which is a time of minimum infestation, must have some effect upon the health of the rabbit population, it appears that in epidemic years, the numbers increase to such an extent that pneumonia sets in, accompanied by other secondary diseases.

*Passalurus nonanulatus*

*Passalurus nonanulatus* is a small white nematode sometimes found in large numbers in the large intestine of the rabbit. It occurs in 10.7% of the rabbits examined. In a few cases the large intestine had been found to be almost solid with these worms, rendering it impossible to make an accurate count which sometimes ran into many hundreds. It no doubt feeds upon the food materials in the gut and it does not have any serious pathological effects upon its host, except by the removal or absorption of food or possibly by the secretion of toxins (about which nothing is known).

*Eimeria*

This coccidium is undoubtedly a dangerous protozoan. It is an intracellular parasite, developing chiefly in the epithelial cells of the small intestine, and may when present in large numbers give rise to acute enteritis. The oocysts are readily detected in the feces. Infestation though quite common was not usually severe; it was certainly present in 40 out of 50 rabbits, and it is quite probable that the percentage of infestation may have been higher. Wenyon (17) in regard to this parasite states, "Young rabbits are especially liable to infection, and they frequently die in large numbers from acute hepatitis, which is caused by the active multiplication of the coccidium in the biliary epithelium. When an outbreak occurs in epidemic form there may be a high rate of mortality. If the animals survive the acute stage, as they not infrequently do, the infection becomes of a chronic type, and it is found that the infection still persists but is limited to certain areas of the liver, where the bile ducts have been dilated to form white nodules, which may have a diameter of half an inch or more. Infection is spread by oocysts which escape into the

intestine and are passed in the feces". In regard to the enteric form the symptoms ascribed to coccidiosis are chiefly of an enteric or dysenteric character.

#### DISCUSSION

With the exception of *Cittotaenia pectinata* and *Passalurus nonannulatus*, it appears that any one of the parasites discussed is capable of producing sufficient pathogenic conditions necessary to produce an epidemic. The most important of these however are *Nematodirus triangularis*, *Synthetocaulus leporis* and the two species of *Eimeria*. These three forms are undoubtedly capable of producing epidemic conditions. During the survey sufficient numbers were not found to cause epidemic conditions, with the possible exception of *Synthetocaulus leporis*.

Experiments have shown that a free larval form exists in the case of *Synthetocaulus leporis*, and that a similar form probably exists in the case of *Nematodirus triangularis*. In the cases of both these species infestation depends therefore upon the amount of moisture present in the soil. It is also well known that in the breeding of tame rabbits damp or moist conditions favor the development and percentage of infestation of *Eimeria*. It appears therefore that these three parasites are capable of producing pathogenic conditions sufficient to cause disease in epidemic proportions, and that they are all favored by wet or moist conditions. The factors, which include rainfall, affecting the percentage of infestation will be discussed in a later part of the paper.

#### The Correlation between Roundworm Infestation and Metro-topographical Factors

It is well-known that the eggs of parasitic roundworms when outside the host require moisture before development can proceed. Lack of moisture, on the other hand, retards or prevents development, and after a limited time the eggs may fail to hatch even when placed in a suitable environment. Such is the case in forms in which infestation is direct, such as *Trichuris* and particularly in the case of strongyloid worms, which have a free-living larval stage.

Neither the life history of *Synthetocaulus leporis* nor *Nematodirus triangularis* have been completely worked out, but it is definitely known that a free-living larva occurs in the case of *Synthetocaulus* and that possibly a similar form occurs in the case of *Nematodirus*; thus we know that we are dealing with a *soil pollution* infestation.

The conditions necessary for the development of strongyloid larvae in nature usually are suitable food and temperature, the presence of a certain degree of moisture, and as secondary factors affecting the percentage of eggs that hatch, the type of soil and vegetation.

The domestic range of the rabbit is very small (12). Each individual has its own little territory which varies in extent with the topography. In very thick woods it may not exceed 20 or 30 acres, and in bush country perhaps not more than 50 or 60 acres. Very little migration outside this range takes place, and as a result the rabbit is an excellent animal for the study of the factors which affect the percentage of infestation by roundworms.

In determining the relation of meteorological and soil factors to the percentage of infestation it must be remembered that rainfall and temperature over the area are much more uniform than are the types of soil, which may vary considerably even in a small area. Vegetation also varies with the soil and must therefore be considered as varying within these same small limits. The rainfall is probably more important than the types of soil, since it determines to a large extent the surface soil that exists in any one area.

For convenience of discussion the province of Manitoba may be divided into two main areas; a timbered area lying north and east of the line *ab* (Fig. 12); and a southern portion almost totally without timber or scrub lying south of the same line. The area to the south of this line is divided into five zones; each one constitutes a distinct soil province (4). Zone 4 has been enlarged and Zone 5 reduced an equal amount from that given by Ellis (4).

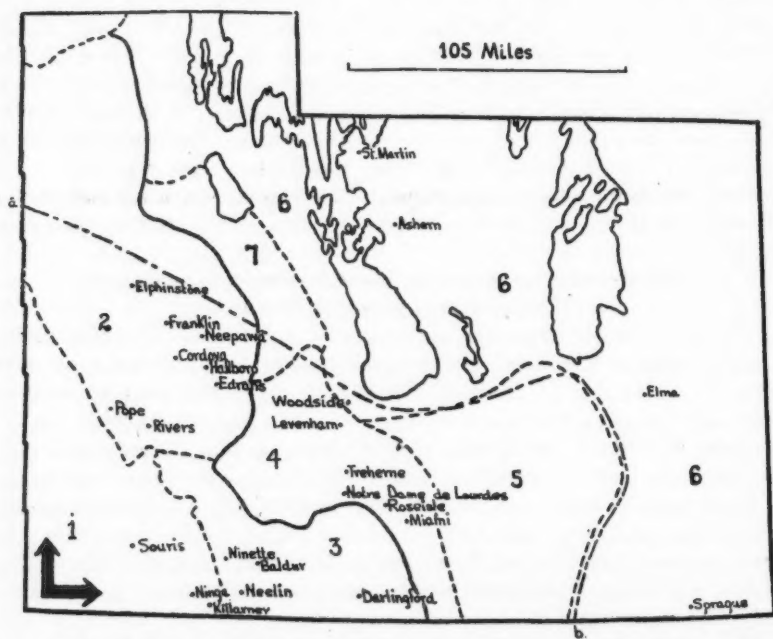


FIG. 12. Map of the lower third of the province of Manitoba, showing the different soil zones. Arrows indicate direction of increase in Nematode infestation and precipitation and a decrease in temperature.

Zone 1 lies in the extreme southwest of the province. The rainfall is below the average for the province; 8.5 in. falls during the period April to July, and 4.6 in. during the period August to October. The temperature on the other hand is above the average for the province. The soil consists of modified drift, sand and dune deposits, with segregated areas of saliferous soil. The vegetation for the most part consists of prairie grasses. The types of soil,

with the low rainfall, hot winds, and moderately high temperature, suggests that this zone would be unfavorable for the development of helminth eggs. This view is supported by the low percentage of infestation in the zone, which is zero in the case of *Nematodirus triangularis*, the hookworm, 5.0% in the case of *Trichuris leporis* and 7.5% in the case of *Passalurus nonanulatus*.

Zone 2 lies to the extreme west of the province and north of Zone 1. The rainfall amounts to 8 in. during the period April to July, and 4.9 in. during the period August to October. The mean temperature is below the average for the province. The drainage is affected by the rolling nature of the country. Basins are formed and, in the years of average rainfall, hold water and form sloughs, which are often surrounded by scrub poplar or willows and offer an ideal habitat for the rabbit. Only the southern portion of the zone has been considered, and this portion consists of two areas; (a) a northern forested area, merging gradually into (b) a southern grass area. Between these two types we find a region in which the trees are invading the prairie, and as a result "islands" of trees occur scattered over the area, giving a park-like appearance. On the whole the soil is close-textured modified glacial drift, and more or less stony. The rainfall, although somewhat below the average for the province, together with the lower temperature, the richer soil, and the greater amount of vegetation provide more favorable conditions for egg development. This is indicated by an infestation of 19.0% in the case of *Nematodirus triangularis*, 8.5% in the case of *Trichuris leporis*, and 12.8% in the case of *Passalurus nonanulatus*.

Zone 3 lies to the extreme south of the province and east of Zone 1. The rainfall is considerably higher than in Zone 2; 9.5 in. falls during the period April to July and 5.2 in. during the period August to October, which amounts to just a little above the average for the province. The temperature is also above the average for the province during the whole of the summer. The soil consists of modified glacial drift and small areas of saliferous soil. The vegetation consists of prairie with fringes of scrub on the banks of the streams. The topography is undulating to rolling and the drainage on the whole is good. The soil is very similar to that of Zone 2 but the increased rainfall, which amounts to 2 in. above that of Zone 2, combined with higher temperatures probably forms more favorable conditions for "egg" development than in Zone 2. Infestation amounts to 27.3% in the case of *Nematodirus*, 9.1% in the case of *Trichuris* and 4.5% in the case of *Passalurus*.

Zone 4 lies approximately in the central part of the area lying south of the line *ab* on the map. The rainfall is higher than the average for the province only during the early part of the summer, but considerably lower during the late summer; 8.9 in. falls during the period April to July, and 4.8 in. during the period August to October. Along the eastern border of the area marshy conditions exist, owing to the subsoil water lying near the surface. The zone is the warmest in the province. The topography varies from level prairie to dune-like hills. The central portion of the area is largely dune sand and grades into fertile sandy planes towards the borders. The vegetation consists of prairie grasses and spruce juniper in the sand hills adjoining the Assiniboine

river. The increased rainfall during the early part of the summer, the waterlogged soil and high temperature are favorable for "egg" development, even in a sandy soil (16). The infestation in this zone amounts to 33.3% in the case of *Nematodirus*, 16.6% in the case of *Trichuris*, and 16.6% in the case of *Passalurus*. The comparatively high percentage of infestation in this case is probably due to the fact that rabbits were received from only the borders of the zone, where conditions are more favorable for "egg" development than in the central portion.

Zone 5 lies directly to the east of Zones 3 and 4 and includes the Red River Valley. The rainfall is above the average for the province; 9.8 in. falls during the period April to July, and 5.8 in. during the period August to October. The temperature is higher than the average for the province. The soil is a rich tenacious clay loam of lacustrine and alluvial formation resting on glacial drift. The indigenous vegetation was grassy prairie, with scrub and timber growths fringing the banks of the Red River. The conditions in this zone appear to be more favorable for "egg" development than any of the zones already discussed, but unfortunately no figures are available for the area.

Zone 6 comprises the northern half of the area under discussion, lying north of the line *ab* (Fig. 12). The rainfall is below the average for the province for the early part of the summer, but far above the average for the latter part; 8.1 in. falls during the period April to July, and 6 in. from August to October. The temperature is below the average for the province. The soil is boulder till, modified with lacustrine action, and gravel deposits with a considerable area of peaty soil. The surface soil over a large area consists of "humus", due to most of the area being covered with scrub and timber, which is intermixed with meadow land; a few tamarac swamps occur in the eastern portion and a number of floating bogs in the northwest. The topography is flat and many shallow lakes occur over a large part of the area.

TABLE III  
COMPARISON OF INFESTATION DURING THE WINTER AND SPRING OF 1930-31, AND  
THE METEOROTOPOGRAPHICAL FACTORS

Zone	Rainfall, in.	Type of soil	No. examined	Percentage of infestation		
				<i>Nemato- dirus</i>	<i>Trichuris</i>	<i>Passalurus</i>
1	13.1	Dune and sand deposits	40	0.0	5.0	7.5
2	12.9	Close-textured drift	70	19.0	8.5	12.8
3	14.7	Glacial drift	22	27.3	9.1	4.5
4	13.7	Sandy loam to dune sand	36	33.3	16.6	16.6
5	15.6	Tenacious clay loam	0	?	?	?
6	14.1	Humus and peat	35	42.9	17.2	6.0

The surface soil, which consists largely of humus, and the shaded moist conditions make the area appear exceedingly favorable for nematode egg and larval development. The zone itself comprises an area much larger than was



covered by the present survey, and only the lower portion skirting the other zones has been investigated. It is probable that in this southern part of the zone the temperature would be higher than that given by Ellis (4). The percentage of infestation in this area amounts to 42.9% in the case of *Nematodirus*, 17.2% in the case of *Trichuris* and 6% in the case of *Passalurus*.

Zone 7 lies directly west of Zone 2 and north of Zone 4. This district has been entirely neglected, not only because rabbits were not procured from the area, but also due to the great complexity of the soil, which includes almost, if not all, the types found in the other zones. The occurrence of the various types of soil produces a corresponding complexity in the types and amount of vegetation. The topography, meteorological conditions and the degree of infestation of the various zones are summarized in Table III.

#### DISCUSSION

In general the rainfall in the province increases progressively east and north from the southwest corner, the minimum occurring in Zone 2, and the maximum in Zone 5. Temperatures, in general, decrease progressively north and east from Zone 1, the highest mean temperature occurring in Zone 4 and the lowest in Zone 6. The high temperatures that occur in a number of the zones, particularly in Zone 1 and the central part of Zone 4, are detrimental rather than favorable to parasitic egg development, because with good drainage and excessive evaporation unsuitable conditions for egg development are produced. The north and eastern part of the area, although having a lower temperature, have more favorable conditions, due to the humus and wet conditions produced by the vegetation. The soil varies from sandy in the western part of the province to a rich humus in the eastern part.

Experiments carried out by Stoll (16) showed that the greatest number of *Ankylostoma* and *Necator* larvae were produced from a given amount of fecal material when the nematodes were cultured in humus, and lesser amounts were produced in sand, loam and clay, providing moisture and temperature conditions were equal. In the present survey however, it was found that sandy conditions produced the least amount of strongyloid infestation owing to the excellent drainage properties of sandy soil; maximum infestation was found in Zone 6, which is covered to a large extent by humus.

The incidence of infestation in the case of the roundworms depends upon climatic factors, similar to those stated by Spindler (14) for *Trichuris trichura* and *Ascaris lumbricoides*. Conditions in Zone 1 and the central part of Zone 4 are very seldom favorable for nematode egg development, and this was particularly true during the last two years (1930-1931) which have been regarded as dry years in western Canada. There is no doubt that during the past summer (1931) favorable conditions for egg development did not exist in Zone 1 and the central part of Zone 4.

Although conditions appear favorable for egg development in Zone 5, it is possible that, due to the well-irrigated conditions over most of the zone, the incidence of infestation may be lower than in Zones 3 and 4 in which one would expect a lower incidence of infestation.



The following conclusions may be drawn therefore with regard to the correlation between parasitic incidence and climatic conditions:—

1. From the above discussion it appears that there is a definite relation between the incidence of helminth infestation, and the mean rainfall, mean temperature, soil structure and vegetation.
2. The occurrence of a considerable amount of moisture, which appears to be the main climatic factor favoring helminth infestation, may be brought about by one or by both of two factors; either a heavy annual rainfall, or the presence of a large amount of vegetation which would tend to prevent evaporation and conserve the moisture in the soil when the mean rainfall is low.
3. The incidence of infestation appears to be at a minimum in Zone 1, where the surface soil is sandy, and at a maximum in Zone 6, where the surface soil is composed largely of humus.
4. The incidence of infestation in the case of the strongyloid *Nematodirus* agrees with experiments carried out in the laboratory by Stoll (16), except in sandy soil, which is explained by the exceptional drainage property of sand in nature. Infestation in Zone 4 is explained by the ground water coming to the surface towards the borders of the zone, which is the area from which most of the rabbits were received.
5. The number of rabbits examined was small considering the wide area covered by the survey, and to justify definite conclusions it would be necessary to perform autopsies on many thousands of rabbits, but the writer publishes the information available, with the hope that it may lead to further developments.

#### Acknowledgments

The survey was carried out under the supervision and direction of Prof. R. A. Wardle, to whom acknowledgment is due for his helpful suggestions, kind criticisms, and assistance in the preparation of manuscript.

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## REVIEWS AND NOTES

### DISCUSSION ON "LONGITUDINAL AND RADIAL VIBRATIONS IN LIQUIDS CONTAINED IN CYLINDRICAL TUBES"

*Discussion by C. B. Fisher<sup>1</sup>*

In Field's analysis leading to the equation of radial motion of the tube wall, the following statement appears (2, p. 132):

"In this relation Young's modulus should be corrected to compensate for the fact that the stresses in the tube wall are rapidly alternating, so that the deformation of the wall does not quite attain the statical value corresponding to the instantaneous distribution of pressure in the liquid. Korteweg suggests the following value be used:

$$(19) \quad E' = E \left( 1 - \frac{5h}{6a} \right) \quad "$$

This is hardly justification for any correction of  $E_1$  as the lag in displacement could only be due to the mass of the wall resisting instantaneous displacement. Such an effect occurs, and is taken into account in the differential equation of motion. Korteweg actually justifies Equation (19) in another manner (3, p. 532).

"If we assume that no longitudinal tensions exist, then it is not difficult to take into account, by means of the theory of elasticity, the thickness of the walls,  $A_1$ , in the calculation of  $E_1$ . If  $E_1$  is the ordinary coefficient of elasticity of the tube wall, which also appears in the expansion of a rod of similar material, then

$$E_1 = E_1' \left\{ 1 - \left( 1 + \frac{\lambda}{\lambda + \mu} \right) \frac{A_1}{2R_1} \right\},$$

where  $\lambda$  and  $\mu$  express the two familiar constants (Hülfsgrößen) of the theory of elasticity.

"According to Poisson's hypothesis,  $\lambda = \mu$ , according to Wertheim,  $\lambda = 2\mu$ , which is, however, nearer the truth. If we take Wertheim's relation, then

$$E_1 = E_1' \left( 1 - \frac{5A_1}{6R_1} \right) \quad "$$

That is,  $E_1$  is corrected, not because of the effects of mass in the tube walls, but because when the tube is expanded, even if by a constant internal pressure, the stress is not the same at every point in the tube wall.

Notice also that Korteweg discarded Poisson's hypothesis,  $\lambda = \mu$ , and accepted Wertheim's experimental result, which tended to show,  $\lambda = 2\mu$ . However, later measurements and theoretical studies have disproved the theory that any definite relation exists between  $\lambda$  and  $\mu$ . This is the attitude adopted by Lamb (4, pp. 114-115) and Rayleigh (6, pp. 251-253). A complete outline of the controversy on this point (the so-called "Multi-constant, rari-constant" controversy) is given by Love (5, pp. 12-14).

<sup>1</sup> Engineering Department, Northern Electric Company, Montreal. Manuscript received July 13, 1932.

From results of measurements given by Lamb (4, pp. 114-115) and credited to Everett the following values have been calculated for the factor  $\frac{1}{2} \left( 1 + \frac{\lambda}{\lambda + \mu} \right)$ . Steel, 0.810; wrought iron, 0.775; cast iron, 0.767; copper, 0.878; glass, 0.729. This is the factor taken by Korteweg (and Field) as  $\frac{5}{6}$  or 0.833.

There appears to be, however, a further limitation even on these results. The constants given above can be used only if all particles of the tube wall are vibrating strictly in phase with each other. This condition will hold only if the time required for the wave to travel from the inner to the outer wall of the tube, and return, is small in comparison with the period of the impressed harmonic force. Consider for example a glass tube with a wall 0.2 cm. thick. The time for the wave to travel from the inner to the outer wall and return will be about  $10^{-6}$  seconds which may well be of the order of a period of the impressed force.

The tube now becomes a complicated elastic structure with a secondary high-frequency resonance. The analysis leading to the exact value of the natural periods appears to offer considerable difficulty, and seems not to have been given by Lamb, Love, Rayleigh, Crandall or Timoshenko.

The present writer is indebted to Mr. J. P. Aston of Montreal for the translation of Korteweg's paper.

#### *Discussion by Geo. S. Field<sup>2</sup>*

As pointed out by Mr. Fisher, Korteweg introduced a correction to Young's modulus really to take account of the varying stress in the tube wall resulting from its finite thickness, and I regret that in going over an abstract of Korteweg's paper I did not check this point more closely.

I agree with Mr. Fisher that the correction is in any case considerably in error, and I feel now that it might be better to leave Young's modulus uncorrected, awaiting a mathematical examination of all the factors involved. It is certain that the finite velocity of sound in the tube wall will considerably affect the extension of the wall, and in addition the assumption made by Korteweg that no longitudinal tensions exist is not justifiable, since, with a longitudinal wave travelling down the liquid in the tube, the pressure on the wall is varying in phase continuously along the tube.

For thin walls, the factors mentioned above probably have little effect on the actual transmission of sound in the liquid, but when the wall thickness becomes appreciable in comparison with the radius of the liquid column, such effects may become very appreciable as has been shown by experiment (1).

#### References

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<sup>2</sup> Junior Research Physicist, National Research Laboratories, Ottawa. Manuscript received August 27, 1932.

# A MATHEMATICAL THEORY OF THE GROWTH OF POPULATIONS OF THE FLOUR BEETLE, *TRIBOLIUM CONFUSUM*, DUV.

A CORRECTION OF A PREVIOUSLY PUBLISHED FIGURE<sup>1</sup>

By JOHN STANLEY<sup>2</sup>

In a recent paper (1) the writer developed a function,  $\theta(T, \gamma)$ , descriptive of the number of eggs of age  $\gamma$  at time  $T$  and, in a figure, showed the general form of the frequency-distribution surface.

It appears as a result of further thought that the above-mentioned figure (1, Fig. 1) is somewhat in error. This figure was roughly of the form of Fig. 1 of this present note, the line  $Z$  being the trace of the plane  $\gamma = T$ .

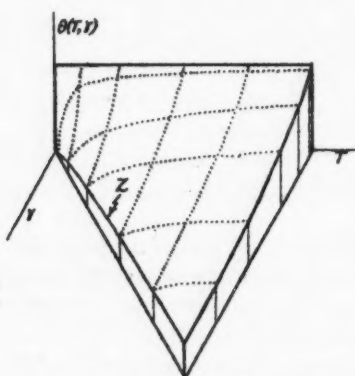


FIG. 1. The frequency-distribution surface  $\theta(T, \gamma)$  as previously shown (1).

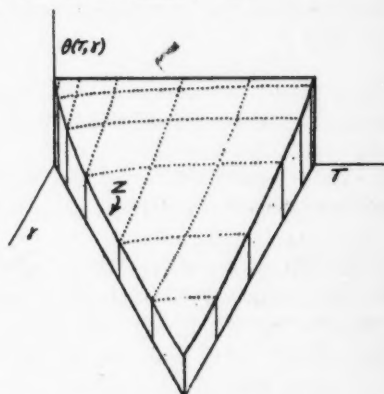


FIG. 2. The frequency-distribution surface  $\theta(T, \gamma)$  as corrected.

However, from (1, Equation 28) it is seen that

$$\lim_{\gamma \rightarrow T} = \lim_{(T-\gamma) \rightarrow 0} \theta(T, \gamma) = ReN_{11} \left[ 1 - \frac{|a|}{b} F(T) \right]^{\frac{H}{|a|}} > 0. \quad (1)$$

This is the equation of the trace  $Z$ , and it can readily be shown that

$$\frac{\partial}{\partial T} \left[ \lim_{\gamma \rightarrow T} \theta(T, \gamma) \right] = -ReN_{11} \frac{H}{|a|} \left[ 1 - \frac{|a|}{b} F(T) \right]^{\frac{H}{|a|}-1} \left[ \frac{|a|}{b} \left\{ \frac{b - |a|F(T)}{cF(T) + d} \right\} \right] < 0, \quad (2)$$

from which it is easily shown that

$$\frac{\partial^2}{\partial T^2} \left[ \lim_{\gamma \rightarrow T} \theta(T, \gamma) \right] > 0. \quad (3)$$

Thus, the trace  $Z$  should be as shown in Fig. 2, rather than as shown in Fig. 1.

## Reference

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<sup>1</sup> Manuscript received November 14, 1932.

Contribution from the Department of Biology, Queen's University, Kingston, Ontario.

<sup>2</sup> Assistant Professor, Department of Biology, Queen's University.

